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Degradation of polymers in unconcentrated and concentrated alkaline urine

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ABSTRACT

Source-separated human urine is a valuable resource rich in plant-essential nutrients, but effective nutrient recovery may require use of chemical additives. This study investigated whether such chemicals can be encapsulated in polymers for passive, controlled release to urine. Degradation of four polymers (polypropylene, polylactic acid, polycaprolactone, polyvinyl alcohol) in $Ca(OH)_2$-dosed urine was assessed, to determine their suitability for encapsulated chemical delivery. Thin films of each polymer were fabricated and exposed to either concentrated or unconcentrated alkalised urine for 16 days, with periodic destructive sampling conducted to assess changes in physical structure and morphology. All polymers demonstrated morphological changes and alterations in molecular weight. Degradation of the polymers resulted in a decrease in pH and an increase in urine COD, indicating significant interactions between the polymers and the urine matrix. Polylactic acid and polyvinyl alcohol underwent the highest degradation in urine and were identified as promising candidates for use in an encapsulated chemical delivery system for treating urine.

1. Introduction

Source separation of urine from the domestic wastewater stream to recover nutrients is important in moving towards a circular nutrient economy (Larsen and Gujer, 1996). Human urine contains macronutrients such as nitrogen (N), phosphorus (P) and potassium (K), and separation enables recycling of these nutrients (Wilsenach and Van Loosdrecht, 2004). Source separation avoids or reduces the need for N and P removal steps in a wastewater treatment plant (Simha et al., 2020; Maurer et al., 2006), where human urine contributes 80 % of the N and 50 % of the P and K found in domestic wastewater (Jönsson et al., 1997).

Urine presents a dichotomy in its environmental impact. As a pollutant, its highly concentrated composition poses a threat to ecosystems, contributing to nutrient overload and eutrophication. As a nutrient resource, its use is primarily hampered by its high water content, which exceeds 95 %. Dehydrating urine to reduce the water content poses various challenges, but also enables researchers to develop novel solutions for recycling the nutrients safely. Various technologies can be used to concentrate the nutrients in human urine (Patel et al., 2020). The most challenging element is N, since a large proportion is excreted as urea that is hydrolysed into ammonia and carbonate, mainly by enzymatic activity in the collection system (Weerakoon et al., 2023). This enzymatic activity can be inhibited by altering the pH of the urine, through either acidification with mineral or organic acid (Simha et al., 2023) or

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alkalisation with alkali earth or metal hydroxides (Hotta and Funamizu, 2008; Randall et al., 2016; Simha et al., 2018; Vasiljev et al., 2022). However, some of the chemicals used in these processes can react with environmental factors (Simha et al., 2024), e.g. pH below 10, leading to reactivation of urease activity. Hydroxides react with carbon dioxide (CO_2) in the air to form carbonic acid, which can decrease the pH of urine to below 10 (Simha et al., 2018). In such instances, additional dosing is required during the dehydration process to raise and maintain the pH at >10 during the entire process.

Continuously adding alkaline chemicals, such as calcium hydroxide, to negate the pH reduction due to carbonation can be difficult in practice. An alternative solution is to use biodegradable polymer pouches containing alkaline chemicals. If pouches dissolve at controlled rates in urine, they would gradually release alkaline chemicals that counter the pH drop due to carbonation during convective evaporation of urine. The degradation rate of polymers in urine likely differs based on their properties, such as thickness, type of polymer and water solubility, as well as the properties of the urine, such as pH, temperature, and ionic strength. To successfully fabricate the pouches, the first step is to identify a suitable polymer that degrades in alkaline urine at a rate sufficient to counter the rate in the drop of pH during evaporation.

Previous studies have investigated the efficacy of passive dosage systems for controlling the toxicity of aquatic environments (Fischer et al., 2024), reducing the turbidity in stilling basins (Bhardwaj and McLaughlin, 2008) and as a pH-sensitive system for the treatment of wastewater (Biltayib et al., 2021). The study by Fischer et al. (2024) investigated the effectiveness of biocompatible polyethylene meshes with high sorptive capacity and fast-release kinetics as a novel passive dosing system to control hydrophobic organic chemicals and dissolved organic carbon (DOC) in test water. The study by Bharadwaj and McLaughlin (2008) used polyacrylamide (PAM) dosing systems to flocculate suspended materials and reduce turbidity in water, while Biltayib et al. (2021) simulated the adsorption removal of cadmium ions from aqueous solutions using a nanocomposite of mesoporous silica structure functionalised with methacrylate and diamine groups. However, to our knowledge, a polymer-based capsulated dosing system for use in source-separated sanitation systems has not been investigated previously.

To develop a polymer-based encapsulated dosing system, it is essential to first identify a suitable polymer based on its degradation dynamics and assess the influence of urine temperature and ionic strength and polymer film thickness on degradation rates. This study aimed to evaluate the degradation of four polymers – polypropylene (PP), polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVOH) – in $Ca(OH)_2$-dosed fresh urine to determine their suitability for fabricating an encapsulated chemical dosing system. PP is a fossil fuel-derived polyolefin with good chemical resistance (Maddah, 2016) and can withstand degradation under abiotic conditions at lower temperatures (Gewert et al., 2015). PLA and PCL are polyesters (Karamanlioglu et al., 2017) and are reported to degrade in abiotic conditions via hydrolysis of the ester bonds (Jamshidian et al., 2010). PVOH was the only water-soluble polymer (Singh et al., 2021) included in this study. These polymers were selected due to their diverse chemical structures and varying degrees of biodegradability, offering a borad perspective on their potential effectiveness for treating urine collected in resource-oriented sanitation systems. Our hypothesis was that PVOH, being a water-soluble polymer, would exhibit the highest degradation rate, followed by the two polyesters—PLA and PCL—due to their differing chemical structures. We also expected the degradation rate to be faster in concentrated urine because the higher ionic strength would facilitate hydrolytic reactions and accelerate polymer breakdown compared to unconcentrated urine. Specific objectives of this study were to evaluate: (i) percentage weight loss and percentage degradation of the polymers in fresh urine dosed with $Ca(OH)_2$; (ii) physiochemical changes in urine due to degradation of the polymers; (iii) changes in the morphology and molecular weight of the polymers during degradation; and (iv) the effect of concentration factor of $Ca(OH)_2$-dosed fresh urine on the degradation rate of the polymers.

2. Materials and methods

2.1. Materials

Fresh human urine was collected from about 30 anonymous donors, both male and female, aged between 20 and 65 years. The donations ($n = 65$) were pooled, dosed with 10 g $Ca(OH)_2$ L^{-1} to prevent enzymatic hydrolysis of urea to ammonia (Randall et al., 2016) and mixed using an overhead stirrer (OHS 60, Velp Scientifica, Italy) for 30 min at 300 rpm. The alkalised urine was kept undisturbed overnight to remove solids and undissolved $Ca(OH)_2$ by sedimentation. The urine was then divided into two portions. The first portion (concentration factor (CF)1 urine) received no other treatment and was used directly in the experiments. The second portion (CF2 urine) was concentrated by evaporation to reduce 50 % of its mass, using a dryer (Daycare DC3600EWL, Electrolux, Sweden).

Laboratory-grade polypropylene (PP) pellets (Merck Chemicals GmbH, Darmstadt, Germany), polycaprolactone (PCL) flakes (Merck Chemicals GmbH, Darmstadt, Germany), polyvinyl alcohol (PVOH) powder (Fully Hydrolysed, Merck Chemicals GmbH, Darmstadt, Germany) and poly L-lactic acid (PLA) pellets (Good Fellow, England) were used to create 2 mm thick polymer films. The PP, PCL and PLA films were made by heat-pressing the polymers at their respective melting temperature, while the PVOH films were made by a solution polymerisation technique, using distilled water as solvent. The films obtained were cut into circles of 2 cm diameter and weighed before use.

2.2. Experimental procedure

Degradation of films prepared from the four different polymers was analysed in the two types of alkalised fresh urine (CF1 urine and CF2 urine) at 20 °C over 16 days. At the start of the experiment, 80 mL of urine and a polymer film were added to glass Petri dishes (diameter 100 mm, height 15 mm; VWR, USA). The control for the experiment consisted of both concentrated and unconcentrated urine without polymer films. The Petri dishes were then placed in closed opaque boxes and kept at 20 °C. At day 2, 4, 8 and 16 of storage in these conditions, the Petri dishes were withdrawn and urine and the polymer films were sampled destructively. The urine samples were collected after filtration using filter paper with pore size 3–5 μm (Grade 390, Ahlstrom Munksjö, Sweden). Solid residues of the polymer films that remained on the Petri dishes were collected by flushing with 50 mL Milli-Q water and filtering through the same filter paper, which was dried at 40 °C for 24 h and finally weighed.

2.3. *Characterisation*

Sample pH was measured using an iUnitrode (6.0278.300, Metrohm Switzerland) connected to a 914 pH/Conductometer (2.914.0020, Metrohm, Switzerland). Soluble COD was determined using a test kit (1.14541.0001, Merck Chemicals GmbH, Germany), on urine samples diluted 10-fold (for CF1 urine) or 20-fold (for CF2 urine) with Milli-Q water.

Simple thermogravimetric analysis was conducted by monitoring the weight loss of virgin polymers and solid residues collected after destructive sampling at different temperatures (100–550 °C) using a furnace (C290, Nabertherm GmbH, Germany). The polymer films were ground to a fine powder, dispersed in tetrahydrofuran and ultra-sonicated for 15 min and then changes in number average (M_n), weight average (M_w), peak (M_p), Z (M_z) and Z+1 (M_{z+1}) molecular weight of the polymers were determined by gel permeation chromatography (GPC) on a Waters® 515 HPLC Pump (Waters Corporation, USA). The results were analysed using the software EMPOWER-2 (Waters Corporation, USA). Scanning electron microscopy (SEM) images were obtained using an electron microscope (JSM 6390LV, JEOL, Japan) at 1000x or 2000x magnification and an area of 4000 μm^2.

2.4. *Calculations*

Percentage swelling, a measure of water intake by a polymer relative to its initial weight (Schott, 1992), was calculated as:

$$Swelling(\%) = \frac{W_s - W_i}{W_i} \times 100 \tag{1}$$

where W_i and W_s are initial weight and swelled-up weight of the polymer film, respectively.

Percentage weight loss of a polymer due to degradation relative to its initial weight (La Mantia et al., 2020), was calculated as:

$$Weight\ Loss(\%) = \frac{W_i - W_f}{W_i} \times 100 \tag{2}$$

where W_i and W_f are initial weight and final weight of the polymer film after drying at 40 °C, respectively.

Poly dispersity Index (PDI), the ratio of weight-average molecular weight (M_w) to number-average molecular weight (M_n) of a polymer (Kissin, 1995), was calculated as (Viéville et al., 2011):

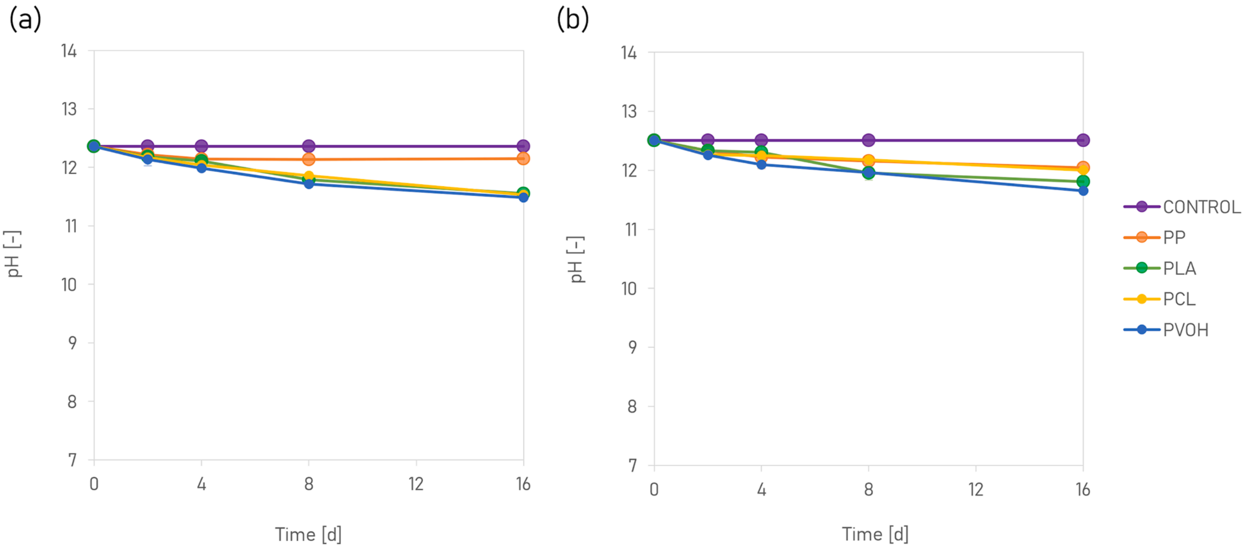

Fig. 1. Change in pH of (a) concentration factor (CF)1 and (b) CF2 $Ca(OH)_2$-dosed urine due to degradation of polymer films (polypropylene (PP), polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVOH)) of 2 cm diameter and 2 mm thickness placed in 80 mL urine at 20 °C and destructively sampled on day 2, 4, 8 and 16. Mean of duplicates (n=2), standard deviation (range ±0.007–0.1) too small to be visible in the diagrams.

$$PDI = \frac{M_w}{M_n} \tag{3}$$

where M_n is calculated based on the mole fraction distribution of different-sized molecules in a polymer and M_w is calculated based on the weight fraction distribution of different-sized molecules in a polymer.

Degradation (%) of the polymer films was calculated based on the change in molecular weight in relation to the molecular weight of the virgin polymer (La Mantia et al., 2020):

$$Degradation(\%) = \frac{M_i - M_f}{M_i} \times 100 \tag{4}$$

where M_i is molecular weight of the virgin polymer and M_f is molecular weight of the polymer after storage in alkalised urine.

2.5. *Statistical analyses*

All experiments were performed in duplicate. Analysis of variance (ANOVA) followed by Tukey's multiple comparison test (Honest Significance Difference, HSD) was carried out to test for significant changes in the physicochemical properties of urine due to degradation of the polymers. All statistical analyses were performed using RStudio version 1.2.5042 and R version 4.0.0 (Team, 2016), with the R-packages car (Fox and Weisberg, 2018) and agricolae (De Mendiburu, 2020).

3. Results

3.1. *Changes in chemical properties of urine*

Degradation of all polymers decreased the pH of alkalised urine (Fig. 1). The average pH decrease was less than one pH unit, with the most significant pH change observed in urine in which PVOH film was stored for 16 days (≈ 1 pH unit). Urine in which PP film was stored showed the smallest change at day 16 (1 % in CF1 urine and 3.5 % in CF2 urine). There was no change in the pH of the controls.

The initial COD concentration in CF1 urine and CF2 urine was 6.12 g L^{-1} and 9.86 g L^{-1}, respectively (Fig. 2). Degradation of the polymers over time increased the COD concentration in urine. In contrast, there was no change in COD concentration in the controls.

At day 16, percentage degradation of the polymer films was higher in CF2 urine than in CF1 urine, as indicated by a greater overall increase in COD in CF2 urine (Fig. 2). Degradation of PVOH film in urine resulted in the largest increase in COD after 16 days, whereas degradation of PCL films gave the smallest increase.

3.2. *Changes in physical and chemical properties of the polymer films*

At day 16, percentage swelling was greatest for the PVOH films (142 % in CF1 and 135 % in CF2) (Fig. 3a, b), whereas for the other three polymers it ranged from 9 % to 15 % (Table S1 in Supplementary Information (SI)).

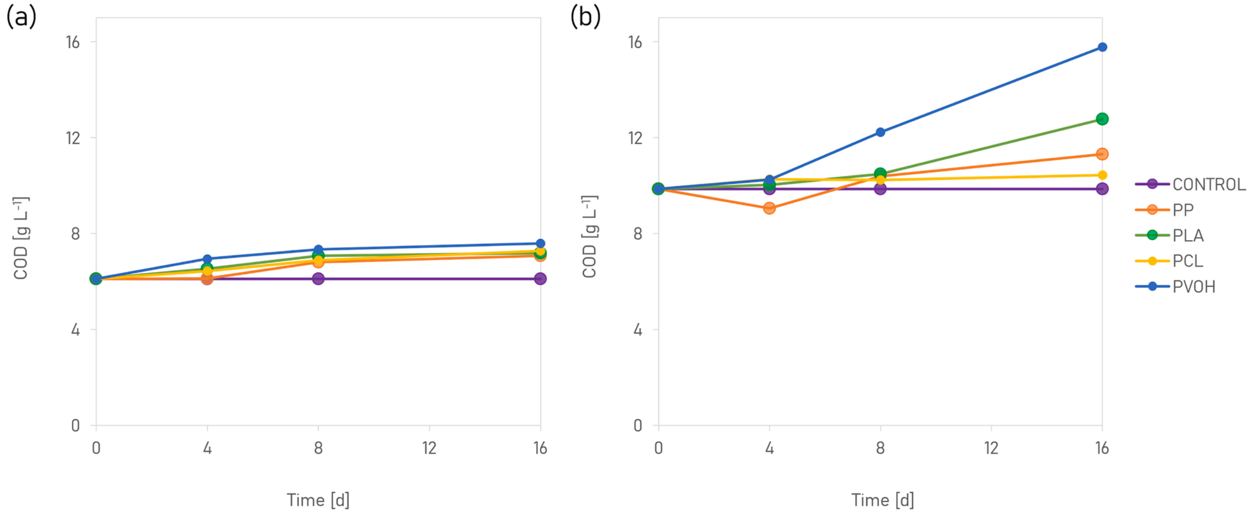

Fig. 2. Change in chemical oxygen demand (COD) of (a) concentration factor (CF)1 and (b) CF2 $Ca(OH)_2$-dosed urine due to degradation of polymer films (polypropylene (PP), polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVOH)) of 2 cm diameter and 2 mm thickness placed in 80 mL urine at 20 °C and destructively sampled on day 2, 4, 8 and 16. Mean of duplicates (n=2), standard deviation (range ±0.03–0.8) too small to be visible in the diagrams.

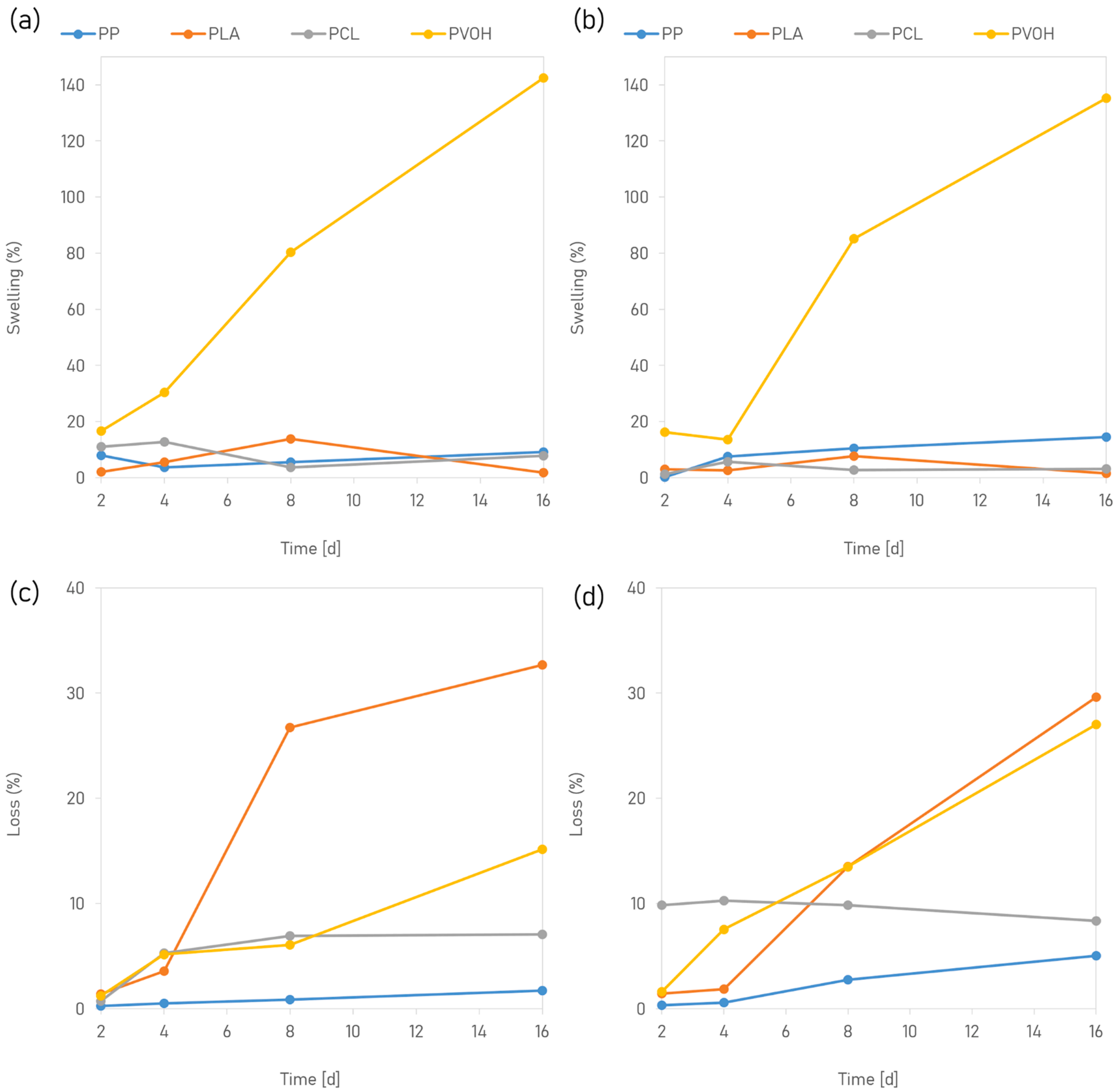

Fig. 3. (a, b) Percentage swelling and (c, d) percentage weight loss (c, d) of polymer films made from polypropylene (PP), polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVOH) and stored in (a, c) concentration factor (CF)1 and (b, d) CF2 $Ca(OH)_2$-dosed urine. Swelling is a measure of water intake by the polymer relative to its initial weight, weight loss is a measure of the reduction in weight of the polymer due to degradation relative to its initial weight. Values obtained in single measurements.

Weight loss was highest for the PLA and PVOH films (Fig. 3c, d). After 16 days, the PLA films lost 30 % (CF1) and 33 % (CF2) of their original weight, while the PVOH films lost 15 % (CF1) and 27 % (CF2) (Table S1 in SI). The maximum weight loss for the PP films was 5 % (CF2), while the maximum loss for the PCL films was 8 % (CF2) (Table S1 in SI).

Weight loss (%) of the polymer films at different temperatures as a function of time of contact with alkalised CF1 and CF2 urine is shown in Fig. 4. PVOH showed the greatest percentage weight loss at 100 °C, followed by PLA. For PVOH films, percentage weight loss was highest at day 16, followed by day 8, day 4 and day 2 (both CF1 and CF2 urine). Absolute weight loss was slightly higher for CF2 urine (Table S2 in SI). For PLA in CF2 urine, percentage weight loss showed a similar to trend to that seen for PVOH, i.e. it was greatest at day 16, followed by day 8, day 4 and day 2. For PLA in CF1 urine, percentage weight loss was similar at day 16 and day 8, and also similar at day 4 and day 2. The PCL films showed very little percentage weight loss at 100 °C (both CF1 and CF2 urine), while for PP the weight loss (%) was higher in CF2 urine.

Compared with the virgin polymer films, there was a decrease in M_n and M_w for all polymer films (Table 1). The PDI of the degraded polymer films also changed (Table 1). The M_p, M_z and M_{z+1} values are shown in Table S2 in SI.

Based on M_n and M_w of the polymer films stored in CF2 urine, percentage degradation of PP film was 7.67 % (number average) and 10.14 % (weight average), that of PLA film was 25.04 % (number average) and 13.23 % (weight average), that of PCL film was 0.26 %

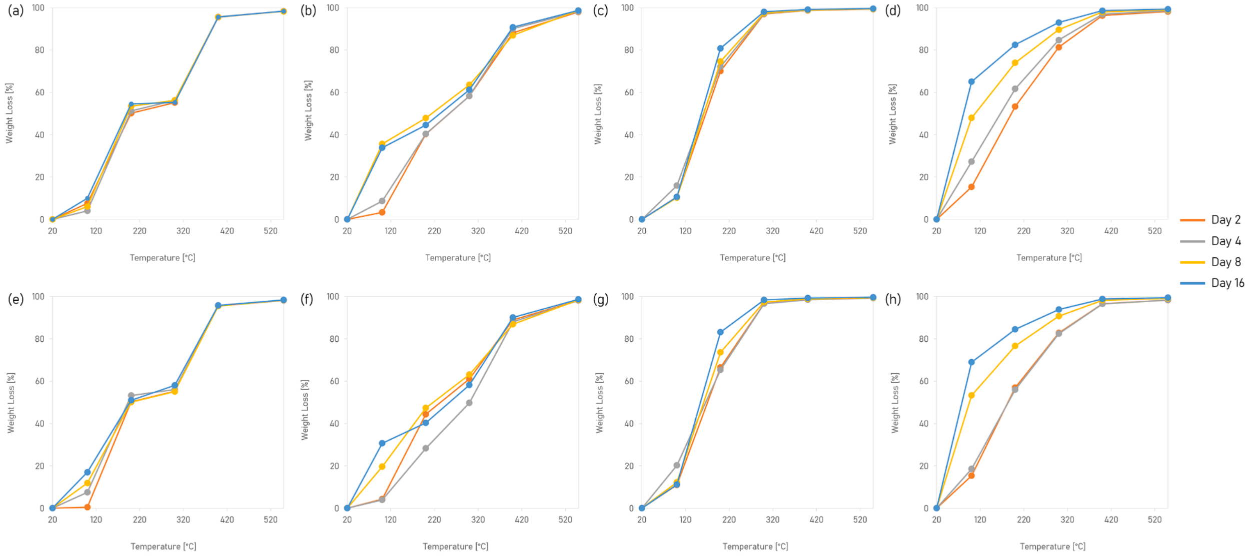

Fig. 4. Weight loss of films made from the polymers (a, e) polypropylene (PP), (b, f) polylactic acid (PLA), (c, g) polycaprolactone (PCL) and (d, h) polyvinyl alcohol (PVOH) and stored in (a, b, c, d) concentration factor (CF)1 and (e, f, g, h) CF2 $Ca(OH)_2$-dosed urine at different temperatures.

Table 1
Change (as determined by gel permeation chromatography) in number average molecular weight (M_n), weight average molecular weight (M_w), calculated poly dispersity index (PDI) and percentage degradation (D %) of polymer films made from polypropylene (PP), polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVOH) and stored in concentration factor (CF)2 $Ca(OH)_2$-dosed fresh urine at 20 °C for 16 days.

Polymer film	Retention time (min)	M_n (Da)	M_w (Da)	PDI	D % for M_n	D % for M_w
Virgin PP	7.83	26671	44751	1.6	-	-
PP in CF2 urine (Day 16)	7.36	24625	40213	1.6	7.67	10.14
Virgin PLA	5.96	131568	188622	1.4	-	-
PLA in CF2 urine (Day 16)	6.16	98614	163657	1.6	25.04	13.23
Virgin PCL	7.23	27071	39978	1.4	-	-
PCL in CF2 urine (Day 16)	7.25	26998	42692	1.5	0.26	−6.78
Virgin PVOH	6.1	126617	151757	1.1	-	-
PVOH in CF2 urine (Day 16)	8.36	80112	80118	1	36.72	47.20

(number average) and 6.78 % (weight average), and that of PVOH film was 36.72 % (number average) and 47.20 % (weight average) (Table 1).

As can be seen in panel (a) in Fig. 5, all virgin polymer films had smooth morphology with minimal defects except for PVOH (Fig. 5a4), which had various imperfections due to escape of the solvent (de-ionised water) as it was made using the solution polymerisation technique. After storage in CF1 or CF2 urine at 20 °C for 16 days, there were visible imperfections in all the polymer films (Fig. 5). The PLA films showed signs of structural breakdown with visible deposits, which were likely a mixture of degraded polymer and precipitates formed in the urine (Fig. 5b2, c2). The PCL films showed signs of marginal swelling after storage in alkalised urine for 16 days (Fig. 5b3, c3).

4. Discussion

The PLA and PVOH films tested in this study showed significant degradation over time when stored in urine, while the PP films exhibited minimal degradation and the PCL films negligible degradation. Degradation of all polymer films resulted in a decrease in the pH of stored urine (Fig. 1). As PP is a polyolefin, it does not easily degrade in abiotic or biotic conditions (Yeung et al., 2021). However, when it degrades under abiotic conditions, this leads to the formation of new functional groups such as carbonyls and hydroperoxides (Gewert et al., 2015). Degradation of PLA in alkaline conditions occurs via hydrolysis of ester bonds, resulting in the formation of lactic acid and alcohol (Södergård and Stolt, 2002). Since PCL is from the same polyester family as PLA, it degrades in alkaline conditions. However, the alcohol that is formed upon degradation of PCL is 1,6-hexanediol and the acid is 6-hydroxylcaproic acid (Leroux et al., 2020). Degradation of PVOH in abiotic conditions leads to the formation of a cocktail of ketones, fatty acids and alcohols (Petkovšek et al., 2023). Overall, therefore, the degradation byproducts from all four polymers were acidic and led to a decline in the pH of stored urine over the 16-day storage period in this study.

Fig. 6 shows the increase in COD of CF2 urine at day 16 as a function of degradation of the polymer films (based on M_n and M_w). As can be seen, there was a positive linear correlation between film degradation and COD level. The PVOH films showed the greatest

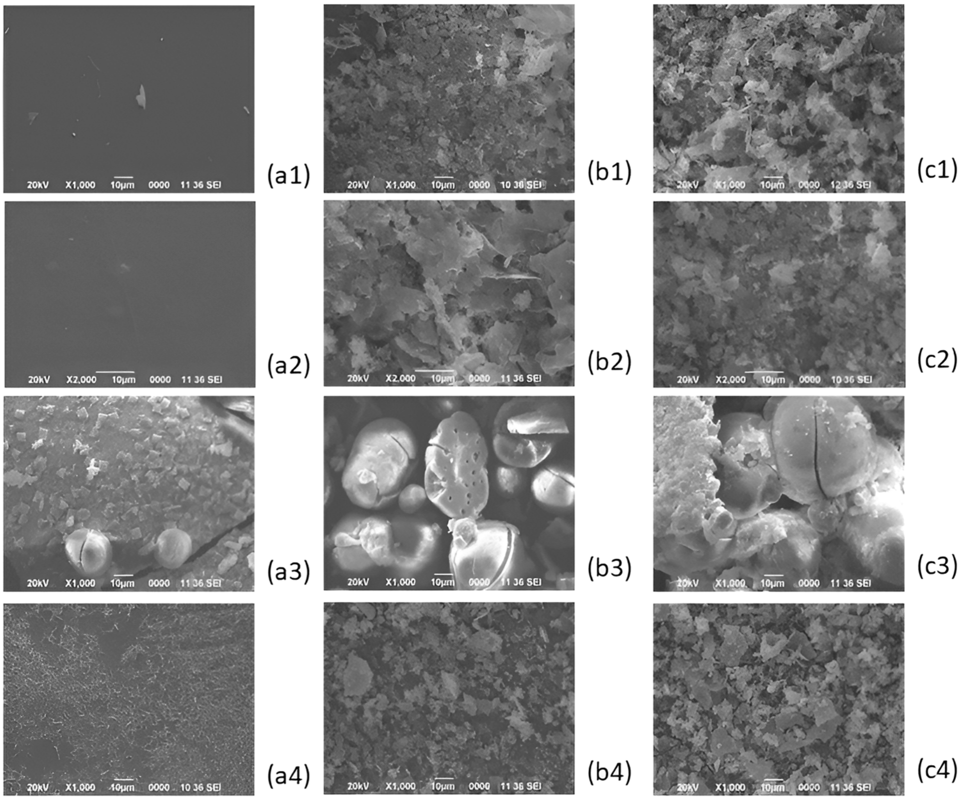

Fig. 5. Scanning electron microscope (SEM) images at 1000x magnification of (a1) virgin polypropylene (PP) film and PP film stored in (b1) concentration factor (CF)1 and (c1) CF2 $Ca(OH)_2$-dosed fresh urine at 20 °C for 16 days (a2) virgin polylactic acid (PLA) film and PLA film stored in (b2) concentration factor (CF)1 and (c2) CF2 $Ca(OH)_2$-dosed fresh urine at 20 °C for 16 days (a3) virgin polycaprolactone (PCL) film and PCL film stored in (b3) concentration factor (CF)1 and (c3) CF2 $Ca(OH)_2$-dosed fresh urine at 20 °C for 16 days (a4) virgin polyvinyl alcohol (PVOH) film and PVOH film stored in (b4) concentration factor (CF)1 and (c4) CF2 $Ca(OH)_2$-dosed fresh urine at 20 °C for 16 days.

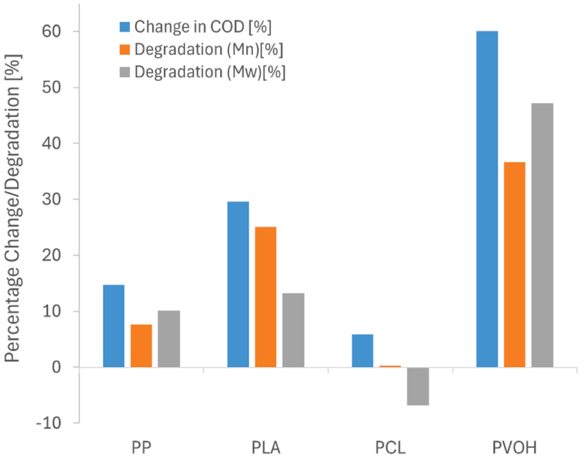

Fig. 6. Increase in chemical oxygen demand (COD) of concentration factor (CF)2 $Ca(OH)_2$-dosed fresh urine and percentage degradation (D %) at day 16 of polymer films made from polypropylene (PP), polylactic acid (PLA), polycaprolactone (PCL) and polyvinyl alcohol (PVOH). Degradation calculated based on available gel permeation chromatography (GPC).

degradation and the greatest increase in COD, while the PCL films showed the lowest degradation and the lowest increase in COD. Degradation of the polymer films stored in CF1 urine was not calculated, as GPC data for these were not available.

PVOH, the only water-soluble polymer tested in this study, showed the highest percentage swelling, e.g. PVOH films stored in CF2 urine showed 135 % swelling at day 16 (Fig. 3). These films also showed 37 % and 47 % degradation, based on M_n and M_w, respectively, which was the greatest percentage degradation of the polymer films tested. Percentage degradation based on M_n reflects breakdown in polymer chain length, while percentage degradation based on M_w reflects a decrease in polymer chain weight (Makino et al., 1986). The swelling of PVOH films occurs mainly due to the formation of hydrogen bonds between the hydroxyl (-OH) group and water in urine (Harpaz et al., 2019). As more water binds to the hydroxyl groups osmotic pressure is generated, which attracts more water towards the polymer matrix (Hassan et al., 2002). After reaching equilibrium swelling, the structural integrity of the polymer matrix is compromised as the intermolecular forces within the chains of PVOH weaken and the chains are separated and dispersed in the medium (Hassan et al., 2002). However, this does not lead to complete degradation and PVOH can be present in the medium for a long time as microplastics before being completely degraded (Petkovšek et al., 2023). The weight loss of PVOH films at day 16 in this study was 15 % and 27 % in CF1 and CF2 urine, respectively.

The PLA films showed the greatest weight loss of the polymer films tested (Fig. 3c, d). PLA degrades under hydrolytic conditions by diffusion of water molecules, which cleaves the ester bonds, thus reducing the swelling but accelerating the degradation (Casalini et al., 2019). PCL has a similar structure to PLA, with repeating ester bonds (Manivasagam et al., 2019). However, the weight loss of PCL was lower than that of PLA, because during degradation of PLA the inner part of the surface degrades faster due to the autocatalytic effect of carboxyl end groups (Deka et al., 2023). In the case of PCL, hydrolytic degradation is low because of hydrophobicity and crystallinity (Kodama, 2013). The interactions between polymer chains and hydroxide ions are more frequent at higher temperatures (Deka et al., 2023), and thus PCL needs a higher temperature than PLA to degrade in identical conditions. PP is extremely resistant to most chemicals and solvents, especially at lower temperatures (Maddah, 2016). Thus, percentage weight loss recorded for the PP films in urine was negligible (<5 %).

Degradation of the polymers, especially the polyesters, was expected to be faster in CF2 urine, where the concentration of salts and ions was higher, since increased ionic strength of the medium accelerates hydrolysis of the ester bond by acting as a catalyst (Visco et al., 2012). This was apparent in the percentage weight loss of PVOH at day 16 (25 % in CF2 urine and 14 % in CF1 urine). Some ions can participate in ion-exchange reactions with functional groups on the polyester chains, leading to structural changes that may facilitate degradation processes (Lee and Gardella, 2000). Salts and ions can affect the water sorption behaviour of polyesters, altering the kinetics of water molecule diffusion into the polymer matrix. Increased water uptake can accelerate hydrolysis and other degradation mechanisms (Lee and Gardella, 2000). Degradation in this study was highest for the PVOH film (36 % and 47 % for M_n and M_w, respectively) (Table S3 in SI), as it was the only water-soluble polymer tested and had the highest percentage swelling, which was caused by its high water intake. PLA film showed the second highest degradation (25 % and 13 % for M_n and M_w respectively) (Table S3 in SI). Despite PLA not swelling as much, the ester bonds were hydrolysed by the salts and ions present in urine. PLA is a bioplastic that is made from renewable plant-based raw materials and produces 80 % less greenhouse gas emissions than conventional plastics such as PET during its entire life cycle (Shen, 2011). A earlier study by our research group showed that degradation of PLA is dependent on pH and temperature, with accelerated degradation at elevated temperature (Deka et al., 2023). Thus, PLA can be used to encase chemicals to treat source-separated urine and other wastewater streams at temperatures below 30 °C for a short period. The degradation rate of PLA is dependent on its crystalline structure, meaning that the less crystalline enantiomer PDLA will degrade faster than the more crystalline enantiomer PLLA in identical conditions (Vieira et al., 2010). Thus, PLLA or PDLA can be used as part of a passive dosage system and the time of release of the chemical load can be controlled depending on the enantiomer selected for use. Disadvantages associated with PLA are its price and permeability. The unit cost of PLA, a bioplastic, exceeds that of fossil-based polymers such as PVOH (Nampoothiri et al., 2010) and it has higher permeability than other plastics, meaning that moisture can pass through it more easily (Rhim et al., 2009). Thus, other polymers such as PVOH will remain structurally intact for a longer period than PLA. If the treatment conditions require a longer-lasting polymer with higher resistance to temperature, PCL can be used instead of PLA. It also has better barrier properties than PLA (Ding et al., 2021).

PVOH is a fossil fuel-based water-soluble polymer (Singh et al., 2021) and its degradation time is dependent on the extent of hydrolysis of the monomers. PVOH takes the longest time to degrade when the monomers are 100 % hydrolysed. In biotic conditions, e.g. in wastewater streams, the multiple breakdown products formed are further converted to acetic acid, hydrogen and carbonate, which can be utilised by methanogenic microorganisms (Wu et al., 2019). Thus, PVOH is better suited for encasing chemicals in order to treat wastewater streams rather than source-separated urine.

Based on the findings in this study, bio-derived polymers from the polyester family, such as PLA, are the best candidates for use in a system that can passively dose chemicals into alkalised urine.

5. Conclusions

Among the polymer films tested, PLA and PVOH films degraded more than PP and PCL films in alkaline urine at room temperature. The maximum weight loss for PLA film was 32 % (CF1 urine), while the maximum weight loss for PVOH film was 27 % (CF2 urine). The maximum degradation for PLA film was 25 % (based on M_n), while the maximum degradation for PVOH film was 47 % (based on M_w). These two polymers also resulted in the highest increase in COD of urine at day 16 (30 % for PLA and 60 % for PVOH, both in CF2 urine). Other results indicated that changes in pH, EC and COD can be used as proxies when evaluating the degradation of polymer films in urine. Doubling the concentration factor of the urine (removing 50 % of the water) did not cause a significant increase in polymer degradation.

CRediT authorship contribution statement

Anuron Deka: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Rupam Kataki:** Writing – review & editing, Supervision, Project administration, Conceptualization. **Prithvi Simha:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Björn Vinnerås:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.eti.2024.103880.

Data availability

Data will be made available on request.

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