Impacts of Potable Water Plastic Pipes Surface Aging on their Lead Deposition Characteristics

Journal:	*Environmental Science: Water Research & Technology*
Manuscript ID	EW-ART-01-2023-000043.R2
Article Type:	Paper

This research investigated the role of surface aging on lead (Pb) deposition onto plastic potable water plumbing pipes. Studying the surface chemistry variations of crosslinked polyethylene (PEX) and high density polyethylene (HDPE) pipes revealed the formation of several oxidized carbon functional groups due to the aging process that promoted lead surface accumulation. This study will inform water consumers, drinking water providers, and the public health sector regarding the potential risk of plastic pipes by providing the resting site for lead, as later, with the water chemistry fluctuation, this surface accumulated lead might be released into the tap water.

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TReceived 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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The application of plastic potable water pipes to replace corroded metallic plumbing and construct new potable water plumbing systems is rapidly increasing due to their low cost, noncorrosive characteristics, and easy installation. However, unlike metallic pipes, knowledge of heavy metals' fate within plastic potable water is limited. This study elucidates the role of plastic pipe surface aging on lead (Pb) deposition characteristics under stagnant conditions. Accelerated aging of crosslinked polyethylene-A (PEX-A) and high-density polyethylene (HDPE) pipes was conducted through exposure to a concentrated chlorine solution at an elevated temperature. Surface chemistry variations of plastic pipes due to aging were examined via attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) analysis. The kinetics of Pb deposition onto the new and aged pipes were studied through 5 d Pb exposure experiments. Moreover, the influence of initial Pb concentration [50-1000 µg/L] on the rate of Pb deposition onto the plastic pipes was investigated. The ATR-FTIR and XPS analysis revealed the formation of several oxidized carbon functional groups [>C-O, >C=O, >O-C=O] on PEX-A pipe and HDPE pipe surfaces after 14 days of accelerated aging. The zeta potential measurement of HDPE pipes showed a slightly more negative surface charge for the aged pipe than the new pipe. The kinetics experiments showed that the aged PEX-A (387 $\mu g/m^2$) and HDPE (418 $\mu g/m^2$) pipes deposited significantly greater levels of Pb compared to the new PEX-A (288 $\mu g/m^2$) and HDPE (335 $\mu g/m^2$) pipes at equilibrium. Pb deposition onto the new and aged PEX-A and HDPE pipes followed a first-order kinetics model implying surface confinement of Pb species. A significantly (p-value < 0.05) greater rate of Pb deposition was found for aged PEX-A compared to the new PEX-A with increasing initial Pb concentration; however, this rate was not significantly (p-value > 0.05) different for new and aged HDPE pipes. This study provides the groundwork for future investigations into the fate of heavy metals in potable water infrastructure.

Introduction

In the U.S., plastic pipes and fittings have been used in water distribution networks for more than 60 years. In new construction and renovations, metallic pipes are often replaced with plastic pipes that are lightweight, inexpensive, easy to install and do not face corrosion problems.[1] Polyethylene (PE) and polyvinyl chloride (PVC) comprise more than 90 % of the plastic materials used for water distribution systems.[2] Crosslinked polyethylene (PEX) and high-density polyethylene (HDPE) pipes are being primarily installed for building potable water plumbing systems and service line connections.[3] Among the three types of commercially available PEX pipes [PEX-A, PEX-B, PEX-C], types A and B are more commonly used for drinking water plumbing systems. The PEX pipe installation rate has increased from 7 % in 2001[4] to 54 % for renovations and 75 % for new building construction in 2013.[5] On the other hand, utilization of HDPE pipes for new building construction has been estimated as 13 %, which was doubled during the last decade.[2]

Although the plastic potable water pipes are not subjected to corrosion, they may get chemically aged as they are used to convey disinfected drinking water. Free chlorine (Cl_2) and chlorine dioxide (ClO_2) are two strong oxidants used to disinfect drinking water. Moreover, chloramine is a widely used disinfectant that is more stable and has a longer-lasting residual effect compared to free chlorine.[6] Previous studies demonstrated that disinfectant residuals present within the tap water could attack and oxidize PEX pipes.[7–9] Antioxidants such as 2,4-Di-tert-butylphenol, and 2,6-Di-tert-p-benzoquinone are added to PEX pipes during the manufacturing process to prevent their oxidation from chlorinated drinking water.[10] However, leaching the antioxidants out of the plastic pipes during the first couple of years of their service makes them susceptible to oxidation by chlorine residuals.[7,8] Field investigations have demonstrated the formation of carbonyl (>C=O) and ether (>C-O-C<) functional groups onto the PEX pipe's surface as a result of exposure to chlorinated water.[9,11]

The polyethylene degradation mechanism was described to initiate with a hydrogen abstraction process, free radicals formation,

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

and generation of peroxyl radicals, resulting in the creation of alcohols, acids, aldehydes, ketones, and unsaturated groups.[12,13] Carbonyl groups on the plastic pipe surfaces are formed due to the chlorine free radicals attacking the pipe material, where hydrogen abstraction is followed by oxygen insertion.[14–16] Plastic pipes exposed to the aqueous free chlorine solution undergo surface oxidation, polymer chain scission, and finally, mechanical failure by developing cracks along the pipe wall.[16] Carbonyl groups are the foremost indicators of polyethylene degradation and the formation of the group on the pipe surfaces exposed to chloramine and chlorine dioxide. HDPE and PEX pipes were found aged with free chlorine at 2 mg/L concentration, which is typically present within the drinking water.[17] In addition to durability issues raised by the oxidation of plastic pipes, the polar surface functional groups created on the plastic surface as the result of this oxidation may alter the physiochemical interactions of the pipe surface with the chemical and microbiological contaminants that are generally present within the tap water, enhancing the risk of their accumulation onto the pipe surface.[3]

Heavy metals could be released into the plastic potable water plumbing system from raw water sources [e.g., Fe, As], treatment practices [e.g., Mg, Mn], water distribution systems [e.g., Fe], and building plumbing systems [e.g., Cu, Pb].[18–20] Previous studies have shown release of metals from metallic pipes and brass fittings through leaching.[21] Metal-plastic hybrid potable water plumbing is commonly found within residential buildings, as existing metallic pipes are partially replaced with new plastic pipes (**Figure 1**). In the case of the complete replacement of metallic pipes with plastic pipes, metallic fittings such as brass connections, valves, and copper elbows are still used.[22] Moreover, many plastics potable water pipes are connected to metallic service lines [e.g., lead, copper]. A recent study reported the metal deposition on downstream PEX pipe due to corrosion of upstream copper pipe and brass fittings.[18] The accumulation of Ca, Mn, and Zn onto the downstream HDPE water mains was reported.[23]

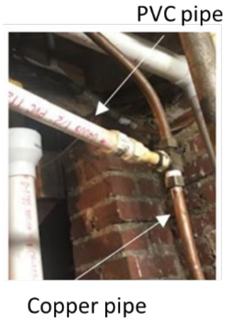


Figure 1. Connection of PVC potable water pipe to copper pipe

There is extensive literature investigating the effect of microplastics' aging on their heavy metal adsorption behavior in the marine environment.[24] However, only a few studies have examined this process under potable water chemistry conditions. The degraded microplastics provided a greater heavy metal adsorption capacity than the virgin microplastics as the degradation alters their physicochemical properties, such as surface functional groups, specific surface area, and zeta potential.[25–27] Heavy metal adsorption varies depending on the plastic type and aging condition.[28–34] Salehi et al. (2017) and Holmes et al. [2012 & 2014] reported increased adsorption of Cd, Co, Cr, Cu, Ni, and Pb onto aged polyethylene compared to new plastic. The oxidized surface functional groups present in the plastic structure were found responsible for the greater metal uptake.[11,32,34] Holmes et al. (2012) reported that the adsorption process achieved equilibrium or new and aged pellets within 25 h to 100 h of exposure duration.[34] Li et al. (2020) demonstrated that UV and chromic acid degraded microplastics adsorbed a greater level of heavy metals than new microplastics.[35] Among various heavy metals that are released by potable water plumbing materials, there is a significant human health concern associated with lead (Pb) exposure through tap water. Lead could be released in dissolved and particulate forms to the tap water depending on its sources, water chemistry, and water flow conditions. Particulate lead is defined as the portion of lead retained by a 0.45 µm filter. The major distinction between particulate and soluble lead is regarding the impact of water flow rate on their release behavior, in which increasing the water flow rate is likely to enhance the particulate lead release, but it reduces the dissolved lead concentration in water.[36,37] A few recent studies have focused on the accumulation of particulate metals onto plastic piping materials. For instance, the study conducted by Cerrato et al. (2006) reported the manganese deposition onto polyvinyl chloride (PVC) and iron pipe materials. A distinct thin brown layer containing particulate manganese (6 % by weight) was found on PVC pipes, which was easily dislodged by flowing water, and contributed to the black water. However, the detachment of particulate manganese was less for the iron pipes due to its roughness compared to the PVC pipes.[38] The study conducted by Gonzalez et al. (2022) solely focused on the physiochemical properties of water that result in $CaCO_3$ scale formation on PVC pipes. However, the role of the pipe's surface characteristics in the scale formation process has not been discussed.[39] The study conducted by Ketrane and Yahiaoui (2021) showed that the $CaCO_3$ scale is forming more in the aqueous phase, than on the surface of HDPE pipes. However, no mechanistic discussion is provided on the role of plastic pipe in providing nucleation sites.[40] Although most of the prior studies focused on the release mechanisms of particulate lead, no attention has been paid to the transport of this particulate matter through the building's plumbing system and subsequent deposition onto the downstream plastic piping materials in distinction with dissolved lead species.

The physical confinement of heavy metals onto the plastic surface and electrostatic interaction and chemical association of heavy metal species with plastic surface functional groups could be impacted by surface morphological and chemical changes caused by plastic degradation and environmental weathering.[41–43] The previous studies demonstrated that oxidized LDPE pellets and films had a higher surface area and hydrophilicity than new LDPE, resulting in a greater Pb^{2+}, Cu^{2+}, Mn^{2+}, and Zn^{2+} uptake from water.[3,43] Mao et al. (2020) studied the adsorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, Ni^{2+}, and Zn^{2+} onto the new and aged polystyrene (PS) and reported an increased adsorption capacity as a function of aging intensity. This could be attributed to changes in the PS's physicochemical features, such as surface roughening and the emergence of oxygen-containing groups on the PS surface.[26] Evidence from the plastic pollution literature also showed that other plastics such as HDPE and PVC sorb heavy metals.[34,44] However, information regarding the influence of plastic pipe surface aging on the heavy metal deposition on their surface is lacking. Thus, this study aimed to investigate the influence of plastic pipe surface oxidation on Pb deposition behavior for PEX-A and HDPE pipes. The specific research objectives were to (1) examine the surface chemistry changes of plastic pipes due to aging in the presence of chlorine, (2) investigate the kinetics of Pb deposition onto the new and aged plastic pipes, and (3) identify the influence of Pb initial concentration on the rate of its deposition onto the plastic pipes.

Experimental

Materials

Cross-linked polyethylene-A (PEX-A) and high-density polyethylene (HDPE) pipes were purchased from McMaster-Carr, USA. The internal diameters of PEX-A and HDPE pipes were 1.7 and 2.1 cm, respectively. Lead (Pb) ICP-MS standard (1000 mg/L in 3 % nitric acid) was purchased from RICCA Chemical Company (Arlington, TX, USA). The 7.1 % sodium hypochlorite (NaOCl) solution was obtained from a local store (Memphis, TN, USA). Nitric acids (68 % purity) were purchased from Fisher Scientific (Hanover Park, IL, USA). All the experiments were conducted using Ultrapure Milli-Q™ (18 MΩ.cm) treated water unless described otherwise.

Pipe Disinfection and Accelerated Aging Experiments

The PEX-A and HDPE pipes were rinsed with tap water and disinfected with chlorinated water to clean the manufacturing residues prior to the experiments. For this purpose, the pipes were filled with approximately 100 mg/L as total Cl_2 solution prepared using tap water and kept for 24 h at room temperature.[45] Then, the chlorinated waters were dumped, and pipes were rinsed with tap water and ultrapure water. The accelerated aging process of the plastic pipes was conducted by filling the plastic pipe segments with 5000 mg/L as total Cl_2 chlorine water at 70 °C, at pH 6.5 for up to 14 d. This solution was made by the addition of 1.4 mL of NaOCl solution (7.1 %) to the tap water. Its total chlorine concentration (the summation of free and combined chlorine) was measured using the Hach Pocket Colorimeter ™ II and total chlorine DPD reagents. The pH was adjusted to 6.5 by the addition of HNO_3 and HCl to the solution. The chlorinated water was stagnant in the filled pipes during this aging process, and the contact water was replaced every 3 d with newly prepared fresh chlorinated water.[46] Filling all the pipes with chlorinated water, both ends of the pipes were sealed with PTFE-wrapped rubber stoppers and placed in an electric oven to maintain the temperature of 70 °C. After 7 d, some of the pipe sections were collected for ATR-FTIR analysis, and the rest of the pipes were removed from the oven after 14 d. Then the chlorinated water was dumped from the pipes and rinsed with tap water and ultrapure water prior to further experiments and analysis.

Surface Chemistry Characterizations

(a) Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy: The ATR-FTIR absorption spectra were acquired by a Perkin-Elmer Universal ATR-FTIR spectrophotometer from 4000 to 400 cm^{-1} with 8 cm^{-1} spectral resolution. Polymer oxidation has been frequently estimated using the intensity of carbonyl and vinyl bonds.[47–50] In this study, the extent of the pipes' surface aging was examined by determining the development of carbonyl and vinyl groups at wavenumber 1715 cm^{-1} and 909 cm^{-1}, respectively.[49,51] Using Equations (1) and (2), carbonyl index (CI) and vinyl index (VI) values were determined, where A_{2870}, A_{1715}, and A_{909} represent the absorbance of methylene (>CH_2), carbonyl (>C=O), and vinyl (>CH_2=CH_2<) functional groups, respectively.[48,49]

$$\text{Carbonyl index (CI)} = A_{1715}/A_{2870} \quad (1)$$

$$\text{Vinyl index (VI)} = A_{909}/A_{2870} \quad (2)$$

(b) X-ray Photoelectron Spectroscopy (XPS): The X-ray photoelectron spectroscopy (XPS) quantifications were accomplished by a Thermo Scientific K-Alpha XPS equipped with a monochromatic Al Kα radiation (hυ = 1486.6 eV). The X-ray source operating power was 75 W at 12 kV, and the analysis area was 400 μm^2 for each sample. During the experiment, the analysis chamber base pressure was maintained at 8.0 x 10^{-10} mbar. The instrument was calibrated to maintain binding energy 284.6 for the C 1s adventitious (aliphatic) carbon line that appears on the non-sputtered samples. Photoelectrons were accumulated from a 90^o take-off angle relative to the sample surface. The survey spectra were taken with a pass energy of 200 eV, and the high-resolution spectra were taken at 40 eV, with 0.1 eV energy step size, using an average of 40 scans. The XPS data analysis was accomplished using Thermo Avantage Software v5.995. Gaussian Lorentzian peaks were used for fitting all the core-level experimental data, and Shirley backgrounds were used as background corrections.[3,52]

Zeta Potential Measurement

Zeta potential measurements were carried out on new and aged HDPE pipes to determine how the surface charge of the plastic pipe fluctuates because of pipe surface degradation. The measurements were conducted using an electrokinetic analyzer (SurPASS, 2010 model, Anton Paar USA, Ashland, VA). To mount the sample for analysis, special adapters were created to fit the inside diameter of the pipes and link them with the outer diameter of the fluid nozzles on the analyzer. The pipe was then squeezed into a narrow channel by being clamped between two custom-made metal bars, about six inches (15 cm) long (**Figure SI-1**). A beaker containing a 500 mL solution of 1 mM KCl was fed to the instrument. Between 50 and 200 mL of the solution was pumped through the channel while the flow ramped up gradually to a pressure of 300 mbar. An electrical current was induced as a result of the interaction between the inner pipe surface and the electrolyte solution, which produced an electrical double layer.[53] The zeta potential was calculated by the instrument software using the current that was observed during the flow rate ramp.

A titration was carried out automatically. The zeta potential was first measured at the original solution pH (typically between 5.5 and 6). Then small doses (~0.1 mL) of 0.1 N HCl were added to the solution until the pH dropped by at least 0.3 pH units. The zeta potential was assessed four times (twice in the forward flow direction and twice in the reverse flow direction). The pH was adjusted again, and the zeta potential was measured again. This continued until the pH of the solution reached almost 3. The solution was replaced with a fresh 500 mL of 0.1 mM KCl, and a similar titration was carried out using 0.1 N NaOH until the pH was close to 9. The titration and testing process took three to four hours in total. A titration curve of zeta potential against pH between 3 and 9 was produced using the combined data from the two experiments.

Metal Exposure Experiments

The new and aged PEX-A and HDPE pipes were cut into 30 cm segments for Pb exposure experiments. Synthetic tap water was used; the constituents of synthetic tap water are mentioned in **Table SI-1**. For the kinetics experiments, 18 pipe segments were utilized to have three replicates for 6-time intervals (2, 6, 12, 24, 48, and 120 h). They were filled with 300 μg/L Pb solution at pH = 7.8. To examine the conditions resulting in more serious health concerns, the lead concentrations above the USEPA action level of 15 μg/L were selected in this study. To study the influence of initial Pb concentration on its rate of deposition onto the pipes, three replicate pipe segments were filled with Pb aqueous solution at five concentrations (50, 150, 500, 750, and 1000 μg/L) at pH = 7.8. The solution pH was adjusted using sodium hydroxide (NaOH) and hydrochloric acid (HCl). An Oakton® pH 450 portable pH meter was used to measure the pH of the solutions. To make sure we have a uniform distribution of lead species in the aqueous lead solutions, the solution was mixed thoroughly right before delivering the aliquot to the pipe segments. Pipe ends were sealed with PTFE-wrapped rubber stoppers and were placed horizontally on a benchtop at room temperature during the metal exposure experiments to avoid the potential deposition of lead precipitates on the PTFE caps. For kinetics experiments, three replicates were removed after each time interval, and the solution was collected for Pb quantification. PTFE caps were removed, and solution was gently dumped into a plastic bottle, acidified with nitric acid for 24 h, and then a subsample was collected for metal quantifications.

The Pb uptake by PTFE-wrapped stoppers after 5 d of kinetics experiments was analyzed for a control sample. The results showed that the PTFE wraps of the two stoppers used for each pipe section accumulated 0.5 % of the total amount of Pb exposed to each pipe section after 5 d of metal exposure in the kinetics experiments. Due to its small value, we have neglected this in determining the metal uptake by pipes. However, for the experiments conducted to study the impact of initial Pb concentration, the samples were removed after 48 h, and the solution was analyzed for the Pb quantifications. Concentrated nitric acid was added to make all the solutions a 2 % nitric acid solution for quantifying the remaining Pb in the solutions. The solutions were analyzed using a Perkin Elmer Analyst 400 Atomic Absorption Spectrometer attached to a HGA 900 graphite furnace to quantify the Pb concentrations. Pb calibration curve was prepared using 0, 5, 10, 25, 50, 75, and 100 µg/L of Pb solutions with the coefficient of determination (r^2) value 0.993, and detection limit 10 µg/L. Statistical analysis is described in the supplemental section (**SI-1**).

Kinetics Modeling

The kinetics of Pb deposition onto the new and aged plastic pipes were investigated through the first-order (FO) (**Equations 3-5**) and second-order (SO) kinetics models (**Equations 6,7**).[41,54] The parameters in these equations demonstrate that t is time, q_t is the Pb surface loading at time t, q_e is Pb surface loading at equilibrium, k_1 and k_2 are FO rate constant and SO rate constant, respectively. The half-life, $t_{1/2}$, is the amount of time needed for the pipe to deposit half of the equilibrium Pb surface loading.[40] The FO kinetics model best describes physical adsorption. It assumes that the rate of the deposition of solute onto the adsorbent is proportional to the difference between saturation surface loading and the amount of adsorbed solute over time, as shown in **Equation 3**. But the SO kinetics model best describes chemical associations between adsorbents and adsorbate species during the adsorption process.[55] The SO model assumes that the rate-controlling step is the chemical association between the solute and adsorbate surface functional groups.[24] Chi-square (χ^2) was employed as a goodness of fitting test by comparing the equilibrium adsorption data from the experiments and calculated from the models (**Equation 8**).[56] The parameters $q_{e,exp}$, and $q_{e,m}$ are experimental and calculated model equilibrium adsorption data, respectively.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{3}$$

$$q_t = q_e(1 - e^{-k_1 t}) \tag{4}$$

$$t_{1/2} = \frac{\ln 2}{k_1} \tag{5}$$

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{6}$$

$$q_t = \frac{q_e k_2 t}{1 + q_e k_2 t} \tag{7}$$

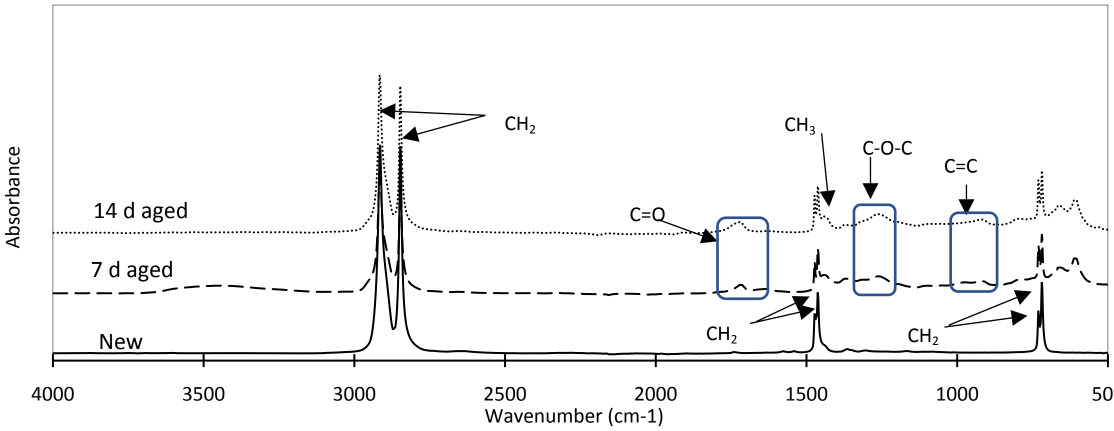
$$\chi^2 = \sum_{i=1}^{n} \frac{(q_{e,exp} - q_{e,m})^2}{q_{e,m}} \tag{8}$$

Results and Discussions

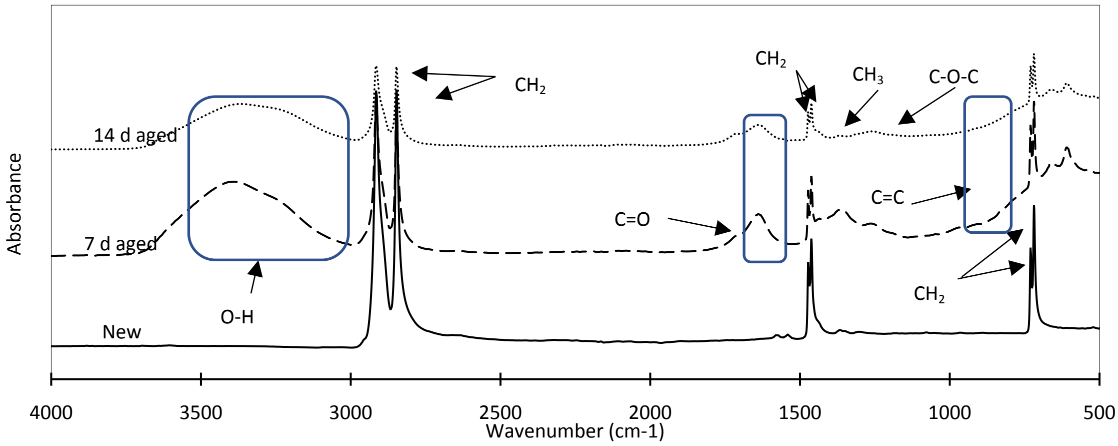
Plastic Pipes Surface Chemistry Variations Due to Aging

(a) ATR-FTIR Spectroscopy: The ATR-FTIR spectroscopy analysis of new and aged plastic pipes revealed significant variations in PEX-A and HDPE pipes due to the accelerated aging process. As shown in **Figure 2a**, the ATR-FTIR characteristic bands of new PEX-A pipes are the asymmetric band of >C-H stretching at 2915 cm^{-1}, a symmetric band of >C-H stretching at 2846 cm^{-1}, $>CH_2$ symmetric bending vibrations at 1470 cm^{-1} and $>CH_2$ asymmetric bending vibrations 1465 cm^{-1}. Moreover, the bending vibrations of $>CH_3$ appeared at 1370 cm^{-1}, and the rocking vibration of $>CH_2$ was found at 730 cm^{-1}.[57,58] For the PEX-A pipe that underwent 7 d of accelerated aging, the new peaks appeared at 1715 cm^{-1}, 1260 cm^{-1}, and 909 cm^{-1}, which indicate the formation of carbonyl (>C=O), ether (>C-O-C), and vinyl (>C=C) groups, respectively, on the inner surface of the PEX-A pipes.[33,59] The presence of >C=O functional group is an important indicator of PEX-A pipe aging and the subsequent formation of aldehydes, ketones, or carboxylic acids on its surface.[33] The presence of vinyl groups at the end of the polymeric chain leads to the chain session.[59] The carbonyl and vinyl indices of the new PEX-A pipe were increased from 0.25 to 0.69 and from 0.27 to 0.82, respectively, after 7 d aging. However, the extent of PEX-A pipes aging remained almost unchanged even if they had undergone an additional 7 d aging under similar conditions. It could be due to the limited strength of the chlorinated aqueous solution in further degradation of the PEX pipe, as suggested by the literature.[60] Whelton et al. (2011) also reported that accelerated aging using 45 mg/L as free chlorine at pH 6.5 for 141 d at 37 °C left no impact on the bulk or surface characteristics of PEX-A pipe.[8] The aging of PEX-A was confirmed by the studies that showed the degradation and even chain sessions occur due to the presence of the oxidized functional groups and unsaturated carbon-carbon double bonds.[11,49,61] Our previous study on exhumed one-year-old PEX-A pipes used for hot and even cold water supply in a residential plumbing system in Indiana revealed that the white PEX-A pipe became yellowish and the oxidized groups such as >C-O-C and >C-O were found on the inner surface of the pipes which confirmed degradation.[33]

The ATR-FTIR characteristic spectra of the new and aged HDPE pipes are shown in **Figure 2b**. The main three methylene ($>CH_2$) group absorption peaks appeared as doublets at 2917 and 2849 cm^{-1} (asymmetric and symmetric stretching), 1472 and 1460 cm^{-1} (bending angular strain), and 730 and 718 cm^{-1} (rocking), respectively.[62,63] The new peaks appeared as a broad hydroxyl (>O-H) at around 3370 cm^{-1}, carbonyl (>C=O) at 1650 cm^{-1}, and vinyl (>C=C) at 909 cm^{-1} due to the HDPE pipe aging.[62,64] The carbonyl and vinyl indices were 0.54 and 0.64 for the new HDPE pipe, and were increased to 0.84 and 1.11, respectively, due to 7 d of aging. By extending the degradation process up to a total of 14 d, unlike PEX-A pipes, the HDPE pipes showed enhanced degradation, demonstrating the carbonyl and vinyl indices increased to 0.95 and 1.12, respectively. Different aging behavior for PEX-A and HDPE pipes due to the increased duration of aging, in addition to their microstructural differences, might be related to the type and percentage of the antioxidants present within their structure. Our results agree with recently published studies that reported the appearance of carbonyl (>C=O) functional group on the HDPE pipe surface due to accelerated degradation (45 mg/L as Cl_2, 50 mg/L alkalinity, pH 6.5, temperature 37 °C, and exposure 141 d).[8]



(a) New and Aged PEX-A pipes

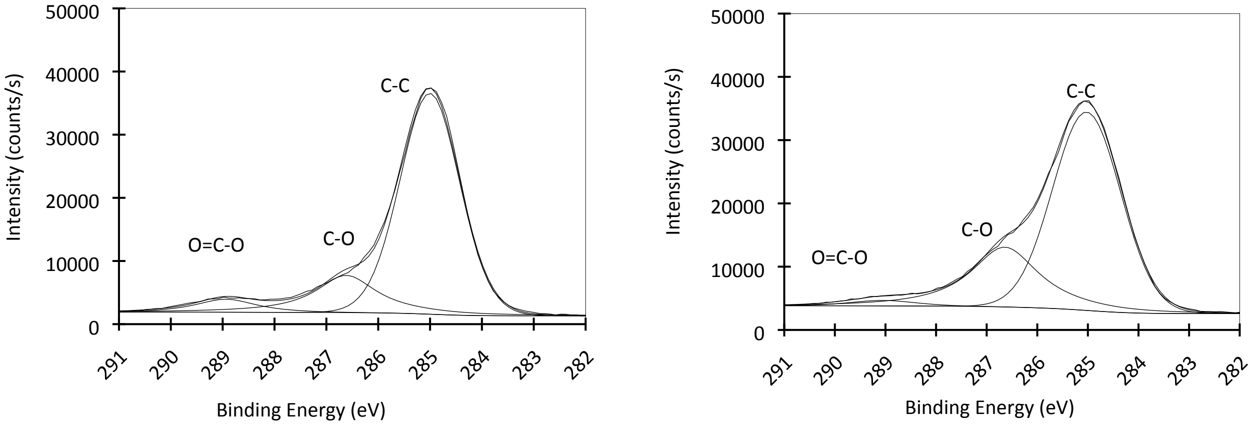


(b) New and Aged HDPE pipes

Figure 2. ATR-FTIR spectra of new, 7 d, and 14 d aged (a) PEX-A and (b) HDPE plastic pipes

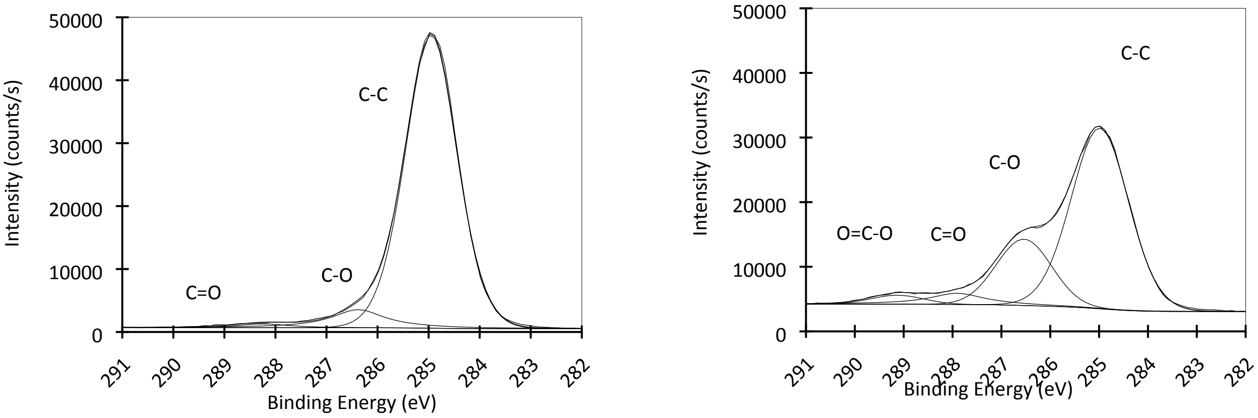
(b) X-Ray Photoelectron Spectroscopy (XPS) Analysis: The XPS analysis was conducted to have a better understanding of the extent of oxidized surface functional groups that were formed on the pipes due to the accelerated aging experiments. Analyzing the XPS survey spectra for the random samples from new and aged PEX-A and HDPE pipes revealed a strong peak at 284.9 – 285.0 eV for the convoluted C 1s and a comparatively weaker peak at 534.1 eV for O 1s (**Figure SI-2**).[18,65] In addition to carbon and oxygen, chlorine was also detected on the pipe surface due to its usage for conducting accelerated aging experiments, although we have rinsed the pipes after aging experiments with tap water and then with ultrapure water. The elemental atomic percentage (%) of C and O was resolved with 0.1 % uncertainty by analyzing the XPS high-resolution spectra (**Table 1**). **Figure 3** shows the deconvolution of C 1s high-resolution spectra into three or four subpeaks (e.g., >C-C/>C-H, >C-O, >O-C-O</>C=O, and >O-C=O).(66) The deconvoluted subpeaks are assigned as >C-C/>C-H, >C-O, >O-C-O</>C=O, and >O-C=O for corresponding binding energies at 284.95 – 285.02, 286.38 – 286.64, 287.91 – 288.25, 288.94 – 289.50 eV, respectively.[65,66] It is possible that the O 1s peaks for these new PEX-A and HDPE are the result of their inherent surface oxidation.[50] As shown in **Table 1**, after 14 d of aging the extent of >C-C< bonds in new PEX-A and HDPE pipes reduced from 80.4 % and 90.7 % to 71.1 % and 67.7 %, respectively, due to the interaction of >C-C< with the chlorine residuals [OCl^-, HOCl] present in the aqueous system, the extent of >C-C< bonds in new PEX-A and HDPE pipes reduced from 80.4 % and 90.7 % to 71.1 % and 67.7 %, respectively, after 14 d of aging.

On the other hand, the percentage of the >C-O< group was increased from 17.6 % to 27 % by 14 d aging of the PEX-A pipes. Moreover, the percentage of >C-O< and >C=O groups increased from 7.8 % and 1.4 % in new HDPE pipes to 24 % and 5.5 % in 14 d aged HDPE pipes. The degree of surface oxidation was calculated using carbon oxidized to unoxidized carbon ($C_{ox/unox}$) and is shown in **Table 1**.[66] The degree of surface oxidation was calculated as the ratio of oxidized carbon to unoxidized carbon (C_{ox}/C_{unox}).[66] A greater degree of surface oxidation was found for HDPE pipes (0.5) compared to the PEX-A pipes (0.4) after undergoing 14 d of the accelerated aging process.



(a) New PEX-A pipe

(b) 14 d aged PEX-A pipe



(c) New HDPE pipes

(d) 14 d aged HDPE pipes

Figure 3. High-resolution deconvoluted C 1s spectra of (a) new PEX-A, (b) 14 d aged PEX-A, (c) new HDPE, and (d) 14 d aged HDPE pipes

Table 1: Elemental atomic concentration percentage of new and aged PEX-A and HDPE pipe samples with 0.1 % uncertainty

Parameters		C 1s				O 1s	Cl 2p	
Samples		C-C	C-O	C=O	O-C=O			C_{ox}/C_{unox}
PEX-A	New	80.4				15.0	4.6	
		77.2	17.6	-	5.2			0.3
	14 d Aged	77.2				9.4	13.3	
		71.1	27.0	-	2.0			0.4
HDPE	New	90.7				8.1	1.2	
		90.8	7.8	1.4	-			0.1
	14 d Aged	73.6				9.3	17.1	
		67.7	23.7	5.5	3.0			0.5

Variations in Surface Charge Due to Aging

Zeta potential measurements were conducted for the representative samples from new and aged HDPE pipes to better understand how surface oxidation of this plastic pipe influences its electrostatic interactions with the Pb species that are present in water. As shown in **Figure 4**, the zeta potential for the new HDPE pipe varied between 0 and -137 mV, however, it varied from -27 to -121 mV for aged HDPE pipe. There was a more negative surface charge with increasing pH, as is typical for virtually all surfaces, due to lower H^+ and higher OH^- concentrations. The presence of oxidized carbon functional groups such as carbonyl (>C=O), ether (>C-O-C<), and carboxyl (>O-C=O<) in aged HDPE surface increase the negative charge. This finding agrees with the results reported by Liu (2021), who also found a more negative surface charge for UV/O3-treated poly (methyl methacrylate) PMMA. The oxygen-containing surface functional groups, specifically carboxyl (>COOH) was presented as the major contributor to the more negative surface charge.[67] Moreover, the study conducted by Asadinezhad et al. (2012) also demonstrated a more negative surface charge for the plasma-treated PVC compared to the new PVC samples due to the presence of a greater level of oxidized carbon surface functional groups [e.g., >C=O, >COOH, >C-O-C<].[68] More negative surface charge may have promoted the electrostatic attraction of neutral and positively charged Pb species to the plastic pipe surface and consequently increases their surface deposition.

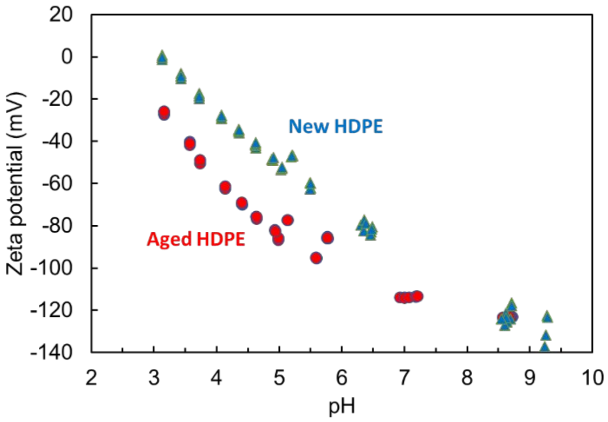
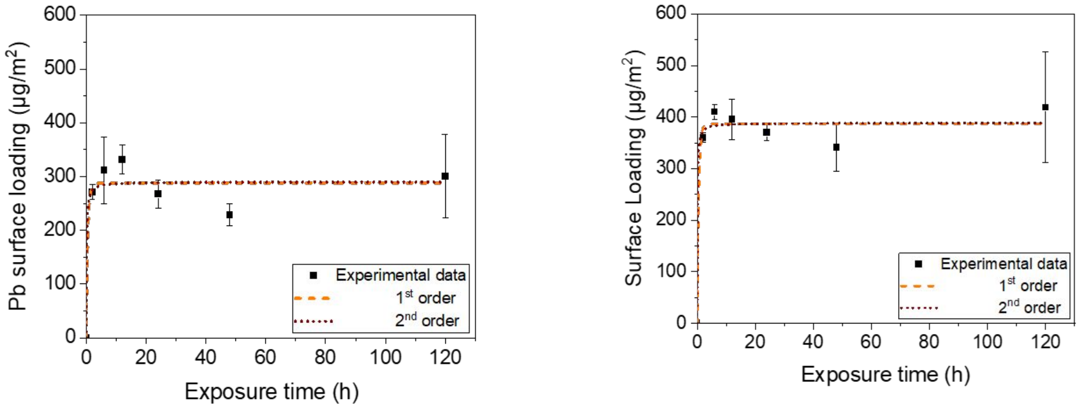


Figure 4. Zeta potential of new and aged HDPE pipes versus pH

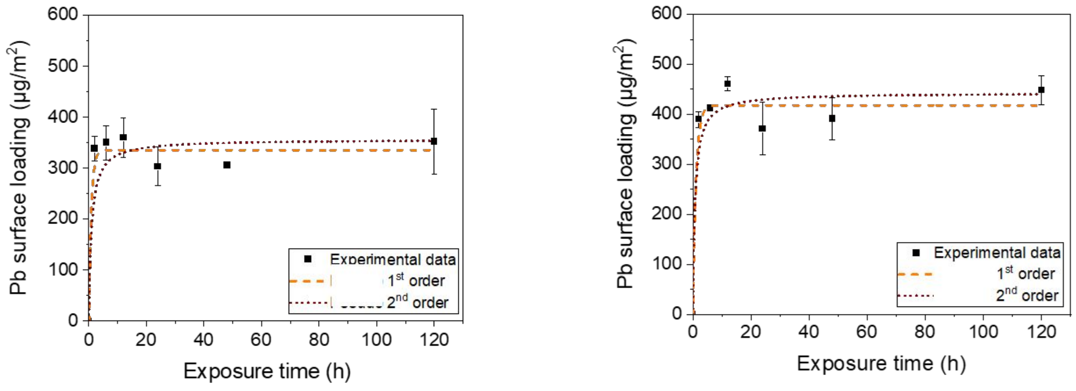
Kinetics of Lead Deposition onto New and Aged Plastic Pipes

The Pb deposition experiments were conducted using synthetic tap water at pH = 7.8 and $[Pb]_t$ = 300 μg/L initial concentration. Solving the relevant complexation and solubility reactions revealed that at this condition 93.55 % of total Pb existed as insoluble species of $Pb(OH)_2$ and the rest were dissolved species. This indicates that for the kinetic experiments in addition to the adsorption of dissolved Pb species into the plastic pipe surface, the precipitation also occurred. Thus, we refer to the Pb uptake by plastic pipe surface as Pb deposition that involves adsorption and precipitation. As presented in our recent research, the metal species initially adsorbed onto the plastic surface could act as nucleation sites for metal crystals to grow.[33] The prior studies have shown that metals could associate with low-energy polymer surfaces such as the attractive local arrangement of polymeric chains, surface impurities, and polymer terminal groups.[69,70] For instance, the nucleation of $CaCO_3$ crystals was facilitated through the complexation of Ca^{2+} with carboxylic acid groups that existed on the surface of grafted HDPE.[71]



(a) New PEX-A pipe

(b) 14 d aged PEX-A pipe



(c) New HDPE pipe

(d) 14 d aged HDPE pipe

Figure 5. First order (FO) and second order (SO) kinetics models for lead (Pb) accumulations onto the (a) new PEX-A (b) aged PEX-A (c) new HDPE, and (d) aged HDPE pipes

Table 2. The kinetics models' parameters and non-linear chi-square (χ^2) values for Pb accumulation onto the new and aged plastic pipes

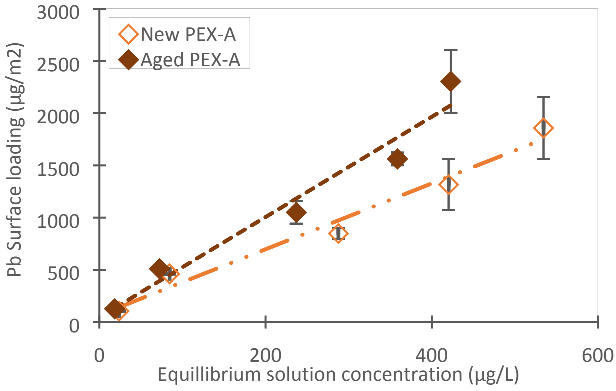
Samples \ Models		1st order				2nd order				q_e ($\mu g m^{-2}$) experimental	χ^2
Parameters		$q_{e,\ model}$ ($\mu g/m^2$)	K_1 (h^{-1})	$t_{1/2}$ (h)	χ^2	$q_{e,\ model}$ ($\mu g/m^2$)	K_2 ($m^2\mu g^{-1}h^{-1}$)	$t_{1/2}$ (h)			
PEX-A	New	288	1.89	0.4	1.88	290	0.030	0.03		265	2.20
	14 d Aged	387	1.91	0.4	0.13	389	0.030	0.03		380	0.20
HDPE	New	335	1.20	0.6	0.12	356	0.003	0.24		329	2.12
	14 d Aged	418	0.91	0.8	0.01	443	0.003	0.24		420	1.17

The kinetics of Pb deposition onto the plastic pipes' surface was examined to better explain how aging and surface oxidation of plastic pipe surfaces alter their physiochemical interactions with the Pb in water. The Pb equilibrium surface loading showed that the aged PEX-A pipes (387 $\mu g/m^2$) deposited a significantly greater (*p*-value < 0.05) level of Pb compared to the new PEX-A pipes (288 $\mu g/m^2$), and the aged HDPE pipes (418 $\mu g/m^2$) also deposited a significantly greater (*p*-value < 0.05) level of Pb than the new HDPE pipes (335 $\mu g/m^2$) (**Figure 5**). During the first two hours of exposure, the aged PEX-A pipe deposited 94.8 % of its equilibrium Pb surface loading, whereas the new PEX-A pipes obtained 94 % of its equilibrium Pb surface loading. On the other hand, during the first two-hour of Pb exposure, the aged HDPE pipes showed a similar trend as new and aged PEX-A pipes, whereas the aged HDPE pipes accumulated 92.8 % Pb surface loading of their equilibrium, and the new HDPE pipe accumulated 100 % of the equilibrium amount. The equilibrium Pb surface loading onto the aged PEX-A pipe was 32 %, whereas the equilibrium Pb surface loading onto the new PEX-A pipe was only 22.1 % of the total Pb $[Pb]_t$ in the synthetic tap water. The aged HDPE pipes accumulated 32 % of the total Pb $[Pb]_t$, like the aged PEX-A, in the synthetic tap water as their equilibrium surface loading, but the new HDPE pipes obtained only 24.0 %. In addition, the comparison with Pb deposition showed the surface loading of Pb onto the new HDPE (335 $\mu g/m^2$) pipe was significantly (*p*-value < 0.05) greater than the new PEX-A (288 $\mu g/m^2$). Similarly, the aged HDPE pipes (418 $\mu g/m^2$) deposited a significantly greater (*p*-value < 0.05) Pb than aged PEX-A (387 $\mu g/m^2$).

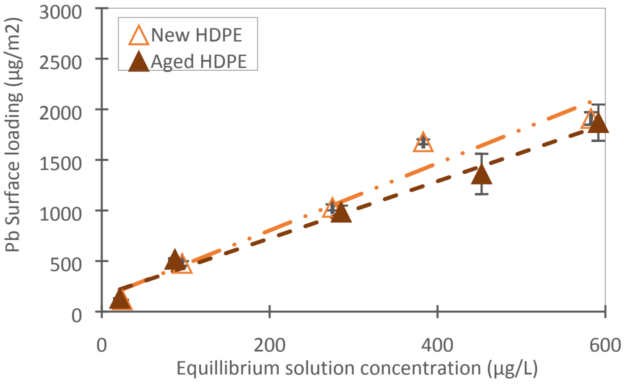
First-order (FO) and second-order (SO) Kinect models were used to describe the Pb deposition mechanisms onto the plastic pipes. FO model demonstrates a more physical process involving diffusion of adsorbate from the aqueous solution to the adsorbent surface.[72] However, the SO model considers the chemical association as the rate-controlling step.[56,73] The non-linear FO and SO models were compared using a nonlinear chi-square (χ^2) test to ascertain which model better suited the kinetics of Pb onto the plastic pipes (**Table 2**). The experimental data of Pb deposition onto the new and aged PEX-A and HDPE pipes were fitted to the non-linear FO and SO models. While the model fits are visually quite similar for the PEX-A pipes (**Figures 5a & 5b**), there is a slight difference in visual fit for HDPE (**Figures 5c & 5d**). The χ^2 values of the FO models were found slightly smaller than SO models for all the studied pipes lending some support to the idea that physical adsorption is a more dominant mechanism than chemisorption. In this study, surface diffusion plays a greater role in Pb deposition onto the pipes rather than rate-controlled chemical association processes as the calculated χ^2 values were so close to each other for the aged pipes using the first order and second order model. The half-life ($t_{1/2}$) calculation revealed that the half-life duration for degraded (0.4 h) and new (0.4 h) PEX-A were similar. However, the half-life for aged HDPE (0.8 h) pipes was slightly greater than new HDPE (0.6 h) pipes.

Influence of Lead (Pb) Initial Concentration on its Deposition Rate onto the New and Aged Plastic Pipes

The influence of Pb initial concentrations on the rate of its deposition onto the new and aged plastic pipes was investigated. At equilibrium, Pb surface loading with respect to the residual Pb concentration remaining in the solution was graphed and slopes were determined as the rate of the Pb deposition. The linear regression revealed, with increasing initial Pb concentration from 50 µg/L to 1000 µg/L, Pb surface loadings on the aged and new PEX-A increased linearly with a very good coefficient of determination (r^2)



(a) New and 14 d aged PEX-A pipes



(b) New and 14 d aged HDPE pipes

Figure 6. Equilibrium Pb surface loading for new and aged (a) PEX-A and (b) HDPE pipes with respect to the residual Pb in the bulk solution.

(**Figure 6a**). The values of the r^2 for aged PEX-A and new PEX-A pipes were 0.96 and 0.97, respectively. The maximum Pb surface loading onto the aged PEX-A pipe was found as 2,304 μg/m^2 greater than the Pb surface loadings onto the new PEX-A (1,859 μg/m^2) but the difference was not significant (p-value > 0.05). However, the rate of Pb deposition onto the aged PEX-A pipes was found greater than the new PEX-A pipes and the difference was statistically significant (p-value < 0.05). This maximum Pb surface loading obtained by our bench-scale experiments is within the range of Pb loadings reported by the field experiments. For instance, the study conducted by Huang et. al. (2019) showed that a six-month-old exhumed PEX-A pipe from a U.S. residential house contained 100 – 135,200 μg/m^2 Pb surface loading.[74] The metal deposition on the PEX-A pipes can be attributed to the possible formation of metal oxides and oxyhydrides at elevated temperatures and a slightly basic system within the potable water plumbing.[74–76]

The Pb surface loading onto the new and aged HDPE pipes increased linearly with raising the Pb initial concentration from 50 μg/L to 1000 μg/L (**Figure 6b**). The r^2 values for aged and new HDPE pipes were r^2 = 0.99 and r^2 = 0.95, respectively. Unlike PEX-A pipes, the maximum Pb surface loading onto the aged HDPE pipes was found as 1,868 μg/m^2 less than the maximum Pb surface loading onto the new HDPE (1,909 μg/m^2), and the difference was not statistically different (p-value > 0.05). Similarly, the rate of Pb deposition onto the aged HDPE was lower than new HDPE pipes, and the difference was not significant (p-value > 0.05). At the lower initial concentrations of Pb^{2+} solutions, the majority of Pb species are present as dissolved species (Pb^{2+}, $PbOH^+$). Thus, surface adsorption is the process that controls the deposition of Pb species onto the plastic pipe surface. However, with increasing the Pb^{2+} initial concentration and exceeding the solubility constants for $Pb(OH)_2$ (s) [K_s*=$10^{8.15}$] the precipitate is formed in the solution and on the inner surface of the plastic pipes. It's expected to have an increasing level of lead precipitates forming in the aqueous system by raising the initial lead concentration. Thus, the lead uptake by water pipes was defined as a deposition to consider both adsorption and precipitation processes. This is relevant to the real potable water plumbing conditions where the pipes are exposed to the particulate lead in addition to the dissolved lead in tap water. The excessive long-term release of lead particulate into tap water may occur by galvanic corrosion or disturbance of the pipe scale caused by partial replacement of lead service lines.[77] Although, in many field investigations, elevated lead levels have been associated with particulate lead, their critical role as the nucleation sites to grow lead precipitate on pipes' inner walls, as shown in **Figure 7**, should not be ignored. As our previous research reported, the metal species initially adsorbed onto the plastic could act as nucleation sites for the metal crystals to grow and precipitate to accumulate on the plastic surface (**Figure 7**).[10] Thus, under a lower range of Pb concentrations, the pipe aging and thus surface oxidation influenced the adsorption of Pb species; however, by increasing the Pb initial concentrations, we had increased layers of insoluble Pb species that are precipitating onto the pipe surface, therefore we did not find a significant difference in the maximum Pb surface loadings for new and aged PEX-A and HDPE pipes.

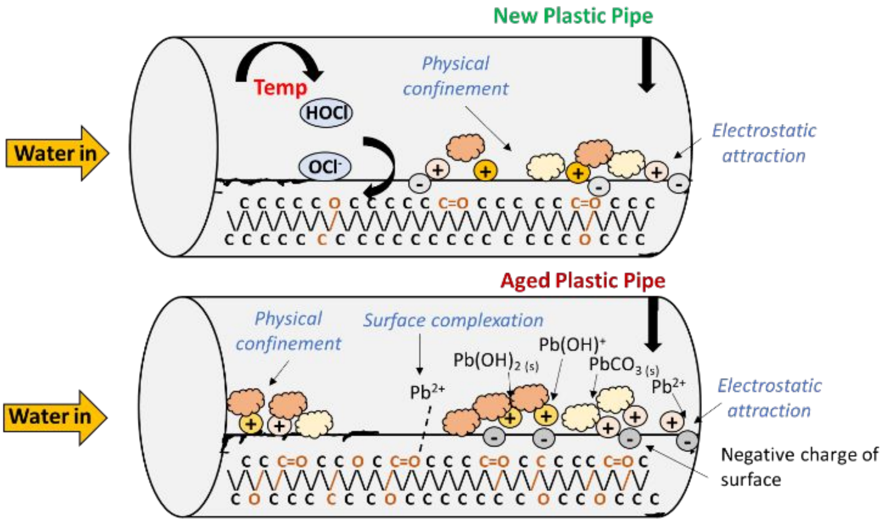


Figure 7. The schematic demonstrating the mechanisms leading to the Pb deposition onto the new and aged plastic water pipes.

Limitations and Practical Implications

This study was associated with some limitations in terms of conducting the accelerated aging process and running the metal exposure experiments only under stagnant conditions. Due to the logistic considerations to complete the aging process within a short duration, the elevated dosage of free chlorine residuals at high temperatures was utilized for the creation of oxidized surface functional groups onto the pipe surfaces.[9,46,78] However, under real operational conditions, the plastic potable water pipes are exposed to a lower concentration of free chlorine (< 2.0 mg/L) at lower temperatures for years. Moreover, although in this study, the Pb exposure experiments were conducted only under stagnant conditions, the plastic pipes used for building plumbing experience both stagnant and flow conditions that vary by the buildings' residents' water use behavior. Shorter contact between the plastic pipes' surface sites and metal species present in the water under water flow conditions and greater mass transfer gradient adjacent to the pipe surface may alter the rate of Pb deposition onto the new and aged plastic pipes.

Moreover, this study showed a rapid deposition of the Pb species onto both new and aged plastic pipes as at least 92.8 % of the equilibrium Pb surface loading on pipes was obtained within the first 2 h of the metal exposure period; however, no metal analysis was conducted during this initial exposure period to capture its early-stage kinetics variations for different pipes. Additionally, the kinetics experiments conducted in this study revealed a rapid uptake of lead by both new and aged plastic pipes. No dramatic increase in the lead surface loadings was found for the target new and aged pipes by increasing the exposure duration from 2 h to 5 d. The mass percentage of lead accumulated on new and aged pipes has not exceeded 24 % and 32 % of the total available lead in the aqueous system, respectively. This finding indicates the limitation of this study as, in real-life conditions, potable water plumbing may be subjected to chronic exposure to lead in tap water for significantly longer durations for those cases with lead service lines or sections of galvanized iron pipes. For instance, it took nearly a year of investigation for several instances in Washington DC (2003) to identify tap water as the source of children's elevated blood lead levels.[79] Thus, future investigation is needed to examine the kinetics of lead uptake by new and aged plastic plumbing materials in long-term exposure experiments. To achieve more representative results of real building potable water plumbing conditions, future studies should consider the interconnected effects of water flow conditions and disinfectant residual decay while conducting long-term lead exposure experiments. Although this study does not distinguish between the interaction of dissolved lead species and particulate lead with the surface of plastic pipes, future research is needed to differentiate the adsorption of dissolved lead species from the surface accumulation of particulate lead. By investigating the interplay between dissolved and particulate lead, researchers can gain a more comprehensive understanding of the mechanisms of lead contamination in plumbing systems and develop strategies to mitigate the risks associated with both forms of lead.

Despite the limitations, this study provides valuable insights regarding the critical roles of plastic pipes' surface aging/oxidation on their association with Pb and, consequently, its transport behavior. Antioxidants are added to the plastic pipes during the manufacturing process to prevent their oxidations due to exposure to the disinfectant residuals in tap water. However, the gradual leaching of antioxidants out of the pipe structure over time makes plastic pipes more susceptible to aging, specifically those pipes carrying hot water. The creation of oxidized surface functional groups on the plastic surface and slight changes in the surface charge impact the physicochemical interactions of the pipe's inner walls with organic, inorganic, and microbiological contaminants present within tap water. Although this study only focused on Pb due to its significant acute and chronic toxic effects, future research is needed to examine how plastic pipe surface aging impacts biofilm accumulation and organic contaminant adsorption onto the pipe surface. These biofilms can interact with heavy metals present in tap water through various potential mechanisms, including metal-mediated alterations in microbial communities, metal-mediated changes in biofilm gene expression, microbial-mediated biosorption, and microbial-mediated metal transformations.[80] Future, systematic investigation is needed to relate the plastic pipe surface chemistry variations to the biofilm growth and heavy metals accumulation in buildings' potable water plumbing systems. Moreover, this study only focused on the deposition of Pb species onto the pipes; future research is needed to identify the physiochemical drivers of Pb mobilization within the plastic potable water system.

Conclusion

In this study, the mechanistic role of plastic potable water pipes' surface aging on Pb deposition onto their inner surface was examined under stagnant conditions. Accelerated aging using high chlorine residuals at an elevated temperature significantly altered the surface chemistry by creating oxidized carbon functional groups [e.g., >C=O, >C-O-C<]. The surface aging and formation of oxidized carbon functional groups made the plastic surface more negatively charged compared to new pipes. The kinetics experiments revealed a significantly greater level of Pb deposition onto the aged PEX-A and HDPE pipes compared to new pipes at equilibrium. The greater electrostatic interactions and potential surface complexations could have promoted Pb deposition onto the aged pipes compared to the new pipes. Increasing the Pb initial concentration resulted in a greater Pb surface deposition onto the new and aged PEX-A and HDPE pipes. A greater rate of Pb deposition was found for aged PEX-A pipes compared to the new PEX-A pipes. The kinetic study revealed a rapid Pb deposition onto the new and aged plastic pipes. The results of this study could serve as a foundation for future studies on the fate of heavy metals in water infrastructure.

Author Contribution

Md Hadiuzzaman: Investigation, analysis, visualization; David Ladner: Methodology, editorial, analysis**;** Maryam Salehi: Conceptualization, Methodology, editorial, Project administration, Funding.

Conflict of Interest

The authors certify that they have NO affiliations with or involvement in any organization or entity with any financial interest or non-financial interest in the subject matter or materials discussed in this manuscript.

Acknowledgment

Funding for this work was provided by National Science Foundation grant CEBT-2029764. The authors thank Colton Kirby and Marvin Dassael Lopez for their assistance with the pipe loop experiments. The authors also thank Dr. Felio Perez for assistance with conducting the XPS analysis and Lingyun Peng for assistance with the surface charge analysis.

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