

Cooking-Induced Corrosion of Metals

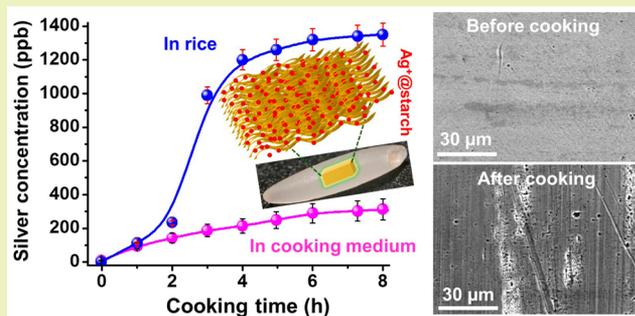
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Supporting Information

ABSTRACT: Uptake of metal ions into rice occurs while it is being cooked in metal vessels, leading to corrosion of the utensils. This study deals with silver, copper, and aluminum uptake during cooking in respective vessels, with a special emphasis on silver. The metal uptake is routed through solution, enhanced in the presence of specific anions like carbonate, and attenuated when the rice is polished. The concentration of silver in rice increases with the time of cooking with a concomitant decrease in the concentrations of Fe and Zn, suggesting a substitution mechanism for metal ion uptake. The results for some common rice varieties of use across the Indian subcontinent are presented. Similar behavior

was observed for cooking in copper and aluminum vessels. Among the three metals studied, aluminum showed reduced uptake. Studies have been done to probe the interaction of metal ions with glucose and sucrose, and efficient complex formation was detected with all these ions, implying that starch can also form complexes with them. The cooking practices used in this study are reminiscent of local customs and practices that were chosen deliberately to relate to the true implications of these results.

KEYWORDS: Cooking, Rice, Corrosion, Silver, Aluminum



INTRODUCTION

While the study of heavy metal uptake by plants has a long history, the presence of the same metals in the human food chain and its dietary implications are relatively recent aspects of study.¹ In this context, it is important to notice that metal ion uptake can happen not only during cultivation but also during processing.^{2–4} Research has revealed the presence of arsenic in rice and other cereals.^{5–7} Spatial mapping of arsenic using secondary ion mass spectrometry (SIMS) has shown that rice bran is the target location for the deposition of arsenic.⁸ Differential uptake of arsenic is observed in various rice cultivars grown in arsenic-rich soil.^{9,10} As even extremely small doses of heavy metals such as cadmium, chromium, lead, and mercury in the diet pose considerable risks to human health,¹¹ their absorption in rice grains is a major public health concern in the entirety of South and Southeast Asia, where rice is a staple.^{12,13}

While rice plants of different cultivars take up heavy metals from the soil, heavy metals may also accumulate in rice during the process of cooking. During cooking of rice, uptake of metals by the rice grains may occur in two ways: from the cooking medium (water) used and from the cooking vessel.^{14,15} The major determinant of uptake during cooking is the chemical property of the metal, especially its affinity for the carbohydrates in rice grains. The aqueous dissolution of various metal species in the cooking medium determines the metal ion concentration in food and its health impacts upon con-

sumption. The chemistry of the carbohydrate on the surface of the vessel, especially at elevated temperatures, can also be a deciding factor for metal uptake. All of these are greatly influenced by the corrosive cooking medium, characteristic of south Asian cooking, composed of acids, typically present in ingredients such as tamarind. In this context, we decided to explore the metal ion uptake during cooking of select food items.

Our study shows that cooking of rice in copper, aluminum, and silver vessels causes corrosion of the surface of the vessels and uptake of the respective metals by rice in the process. While vessels made of copper and aluminum and their alloys are commonly used in a large number of Indian households,^{16,17} the use of silver in cooking utensils was common in wealthy traditional households. Vessels made of silver and copper and its alloys with zinc (brass) and tin (bronze) were traditionally used for storage of water and preservation of food in much of preindependent India.¹⁸ Silver foils are still in use in many parts of India to decorate milk sweets to be consumed along with the sweet.^{19,20} Our selection of these metals is in conformity with the tradition and common practice of cooking in South Asia.

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Table 1. Concentrations (in parts per billion) of Different Metals in Rice Samples, As Purchased from the Market

sample no.	name of the rice	Cr	Mn	Fe	Cu	As	Pb	Sb	Zn	Ag	Al
1	Tamil Nadu Ponni (unpolished, boiled)	432.1	1454.8	3892.4	8380.8	2.3	0.0	3.2	4485.6	11.6	25.2
2	Tamil Nadu Ponni (polished, boiled)	324.6	1442.8	3245.8	7117.2	1.8	0.0	2.4	2681.2	18.4	15.1
3	Karnataka Ponni (unpolished, half-boiled)	298.7	1976.3	3206.0	7546.9	0.0	0.0	2.2	3548.0	13.2	21.5
4	Karnataka Ponni (polished, half-boiled)	245.3	2101.6	2906.2	7280	0.0	0.0	2.8	3419.6	13.5	9.7
5	IR20 (unpolished, raw)	312.4	854.0	1934.5	7052.4	1.5	0.0	2.4	1962	12	7.7
6	IR20 (polished, raw)	243.0	675.4	1743.7	6320.4	1.2	0.0	2.1	1669.9	9.5	3.8
7	Basmati (unpolished, boiled)	332.9	1327.2	2034.1	7844.0	0.0	0.0	4.0	3664	15.2	18.6
8	Basmati (polished, boiled)	309.5	1225.6	1993.4	8549.6	0.0	0.0	5.6	3532.4	18.3	12.9
9	Kerala brown (unpolished, raw)	322.1	958.0	3987.7	4454.8	1.8	0.0	2.0	2109.6	6.8	22.7
10	Idly (unpolished, boiled)	289.8	1184.4	1482.0	8813.6	0.0	0.0	10.4	2297.6	15.2	4.1

METHODS AND EXPERIMENTS

Materials. Metal vessels (purities of >95% silver, >97% copper, and >97% aluminum) were purchased from the local market, to mimic the local cooking practices. The scanning electron microscopy (SEM) images of silver, copper, and aluminum vessels, before use as purchased from the market, are given in Figure S1 along with respective SEM/EDS images (energy dispersive spectroscopy), to determine their chemical compositions. For each metal being tested, three cooking vessels of identical size were used as replicates. Quantitative analysis showed the metal content to be >95% Ag, >97% Cu, and >97% Al (weight percent) in all three vessels of each type, with some oxygen and a small amount of Cu for Ag, Zn for Cu, and Fe for Al vessels (quantitative data are provided in Figure S1). Nitric acid (assay, 69–71%) and hydrogen peroxide [assay, 100%; 30% (w/v)] were purchased from Fisher Scientific. Sodium chloride, sodium carbonate, sodium phosphate, and sodium hydroxide were purchased from Sigma-Aldrich. All 10 rice samples, namely, (1) Tamil Nadu Ponni (unpolished, boiled), (2) Tamil Nadu Ponni (polished, boiled), (3) Karnataka Ponni (unpolished, half-boiled), (4) Karnataka Ponni (polished, half-boiled), (5) IR20 (unpolished, raw), (6) IR20 (polished, raw), (7) Basmati (unpolished, boiled), (8) Basmati (polished, boiled), (9) Kerala brown (unpolished, raw), and (10) Idly (unpolished, boiled), were purchased from the local market and were used without any further treatment. The initial concentrations of various metals in rice are listed in Table 1.

Throughout our paper, “unpolished rice” refers to the decorticated rice grain with an intact bran cover (consisting of pericarp, tegmen, and aleurone layers), whereas “polished rice” denotes decorticated rice from which the bran layer has been removed during milling.

Experimental Procedure. In a typical experiment, 2 g rice samples were placed in Ag, Cu, and Al vessels and cooked in 20 mL of deionized (DI) water at a constant temperature of 80 °C, over hot plates. A glass lid was used in each case to prevent excessive evaporation of water, and for this reason, boiling was not used. A lid and a reduced temperature were used to avoid connecting a reflux condenser on the metal vessel and also because of the former’s resemblance to standard cooking conditions in the region, where the cooking vessel with a lid is heated over a flame. A finite amount of the supernatant was collected at equal time intervals from the same vessel. Initially, 20 mL of water was added in each case for cooking. After every hour, 1 mL of the supernatant was withdrawn for analysis, which was compensated by 1 mL of fresh DI water. Under this optimized condition (arrived at using various control experiments), rice can be cooked in 2 h. The temperature was maintained for longer periods to evaluate the maximal limit of silver uptake by rice. For each metal vessel, experiments were conducted simultaneously in three separate vessels. The vessels were cleaned, and the experiments were repeated thrice for each metal and each rice variety. The nine resulting data points for each metal vessel and each rice variety were averaged.

Antibacterial Test. These tests were conducted with DI water incubated in silver vessels at 80 °C. The bacterial strain used was *Escherichia coli* MTCC 739 (Gram-negative bacteria). *E. coli* was inoculated in sterile nutrient broth and incubated overnight at 37 °C. A 1.5 mL bacterial suspension containing 10^8 colony-forming units

(CFU)/mL of cells was centrifuged (12000 rpm for 1 min), and the pellet was resuspended in 0.8% saline to create a final volume of 1 mL of suspension (final concentration of 1.5×10^8 cells/mL). This mixture was then added to a flask containing 14 mL of DI water containing 70 mg of NaCl, which was used as the control. The concentration of free silver in the samples was kept below the solubility product of silver chloride. The mixture was dispersed in saline for 3 h, centrifuged (12000 rpm for 1 min), and resuspended in 50 μ L of saline. A 5 μ L aliquot of the bacterial suspension was combined with 20 μ L of a fluorescent probe containing 3.34 mM green fluorescent nucleic acid stain, SYTO 9, and 20 mM red fluorescent nucleic acid stain, propidium iodide (PI) [live/dead backlight bacterial viability kit, L7012 from Invitrogen (see below)]. The mixture was incubated in the dark for 15 min, and an ~ 10 μ L aliquot was placed on a 1 mm thick ultrasonically cleaned glass slide (SCHOTT), which was then covered with a coverslip, sealed, and examined under a fluorescence microscope.

Live/Dead Staining Experiment. Live/dead staining experiments are used extensively to discriminate live and dead cells by intracellular staining. The stain utilized is a combination of two dyes, namely, SYTO 9 and PI. SYTO 9 is a green fluorescent nucleic acid stain capable of entering both live and dead cells. The green emission of SYTO 9 is enhanced when it is bound to a nucleic acid and shows a lower-intensity fluorescence signal if unbound. Contrary to this, PI, which is often used as a counterstain, exhibits red fluorescence in multicolor fluorescence techniques and is capable of penetrating only cells with disrupted cell membranes. This red fluorescent nucleic acid stain binds to DNA with no preferential sequence and exhibits 20–30-fold fluorescence enhancement when bound. In cases in which both dyes are used in the same sample, PI exhibits an affinity for nucleic acids stronger than that of SYTO 9, thus displacing SYTO 9 in dead cells where it is capable of penetration.²¹ This in turn leads to depiction of live cells as green and dead cells as red during fluorescence microscopy.

Effects of Silver, Copper, and Aluminum Ions on Humans.

Silver at concentrations in the range of 0.01–0.50 mg/day shows very low toxicity to humans.²² It is widely used as an antibiotic and antibacterial agent for ages.²³ According to the World Health Organization, the maximal permissible limit of silver in drinking water is 0.1 mg/L and the lethal dose of silver salts was found to be ~ 10 g for humans. Excessive exposure leads to deposition of silver on skin, a condition called argyria. Copper is essential for life and is the third most abundant trace element in human body after iron and zinc.²⁴ Many enzymes and proteins contain copper in living organisms. The availability of copper is significant in meats, cereals, and pulses. The safe estimated dietary intake of copper is 0.9–1.5 mg/day.²⁵ The human body has no known requirement for aluminum. Most of the aluminum introduced intravascularly into the body is from drinking water and from conjugates with albumin and is subsequently removed renally. If the aluminum content exceeds the renal removal capacity, it is deposited in various tissues, which might lead to mortal harm.²⁶ The safe limit of aluminum uptake is in the range of 0.10–0.20 mg/day. Excess exposure of aluminum to humans through food causes acute kidney injury²⁷ and neurodegeneration causing Alzheimer’s disease.²⁸ From the reports cited above, it is evident that large scale uptake of

these metals can cause serious health effects. However, uptake of these metals into humans through cooked rice has not been examined in our study.

Instrumentation. We employed an inductively coupled plasma mass spectrometry (ICP MS) PerkinElmer NexION 300X instrument equipped with an argon plasma source for quantification of metals in rice. Silver was calibrated with a silver atomic absorption spectroscopy (AAS) standard solution (1000 mg/L) purchased from Fisher Scientific (product AAAGH). Other elements like Al, Cu, Fe, Zn, and Mn were calibrated by PerkinElmer Instrument Calibration Standard 2 (product N9301721). In all cases, five calibration points were used: 0 (called the blank) 10, 100, 1000, and 10000 ppb. In all the cases, five concentrations of the calibrant were analyzed first until a calibration curve was achieved with an R^2 of 0.9999. After that, the two samples of known concentration (>100 and <1000 ppb) were checked at least three times to obtain reproducible data with a deviation of <0.5 ppb (for samples with concentrations of >1000 ppb). The detection limit for ICP MS is 0.1 ppb for these ions. Blank concentrations of different metal ions in Milli-Q, deionized, and tap water used in the experiment are shown in Table S2.

For analysis, 1 mL of the supernatant (starch) solution was withdrawn at regular time intervals (1 h) and 50 μ L of concentrated nitric acid was added (to yield a 5% acid concentration, which is comparable with the standards of the instrument). For the analysis of metal ion concentration in the supernatant solution during the course of cooking, 1 mL of the solution was pipetted out and the same quantity of DI water was added to the vessel at a time interval of 1 h. After 6 h, the cooked rice was digested for metal ion uptake.

For digestion, 2 g of a rice sample (dry weight) was taken in a Teflon tube and to it were added 5 mL of HNO_3 and 3 mL of H_2O_2 . This mixture was digested using an Anton Parr microwave digester with a power of 800 W, programmed at a ramping time of 10 min, and then it was held for 15 min at 800 W. After cooling, the sample was diluted 10 times with DI water and analyzed using ICP MS. A similar procedure in which the entire amount of cooked rice was digested was followed after the rice had been completely cooked. This is termed “digested rice” in the text. All the experiments were repeated thrice, and an average value is reported. Scanning electron microscopy (SEM) equipped with energy dispersive analysis (EDS) (FEI Quanta 200) was used to record the surface morphology, elemental composition, and elemental mapping of the samples. EDAX Genesis was used to evaluate EDS data. For this analysis, a small amount of the cooked rice was oven-dried and ground into a fine powder prior to analysis. Whole grain was also used for the study without grinding. The ground rice sample was used for laser desorption ionization (LDI) analysis, on an Applied Biosystems Voyager DE Pro matrix-assisted LDI MS instrument. A pulsed 337 nm nitrogen laser was used for desorption ionization. An average of 10 spectra (each spectrum consists of 200 laser shots) were recorded in each case. Electrospray ionization mass spectrometry (ESI MS) analysis was performed using an Applied Biosystems 3200 QTRAP LC MS system in the mass range of m/z 100–1700. The following optimized conditions were used: declustering potential (DP) of 30 V, entrance potential (EP) of 10 V, ion spray voltage (IS) of 2 kV, and collision energy (CE) of 10–100 (instrument units). A 1:1 (v/v) $\text{H}_2\text{O}/\text{MeOH}$ mixture was used as the solvent. XPS measurements were taken with an Omicron ESCA Probe spectrometer with monochromatic Mg $K\alpha$ X-rays ($h\nu = 1253.6$ eV). Most of the spectra were deconvoluted to their component peaks using CasaXPS. The energy resolution of the spectrometer was set at 0.1 eV at a pass energy of 20 eV. The binding energy was corrected with respect to C 1s at 284.5 eV. UV–vis spectra were recorded using a PerkinElmer Lambda 25 spectrophotometer. A Cytoviva HSI system was used for the live and dead staining experiment. Excitation was at 550 nm, and emission was collected using a band-pass filter at 500–550 nm for SYTO 9 and a long-pass filter 590–800 nm for PI. In all cases, measurements were taken using a 100 \times oil (Cargille) immersion objective.

RESULTS AND DISCUSSION

Ten different varieties of rice, including polished and unpolished types, that are commonly used across the Indian subcontinent were selected for our study. While the studies were performed on several varieties, for the purpose of illustration, the uptake in Tamil Nadu Ponni rice, a commonly used native variety, is discussed here. Figure 1 shows a gradual

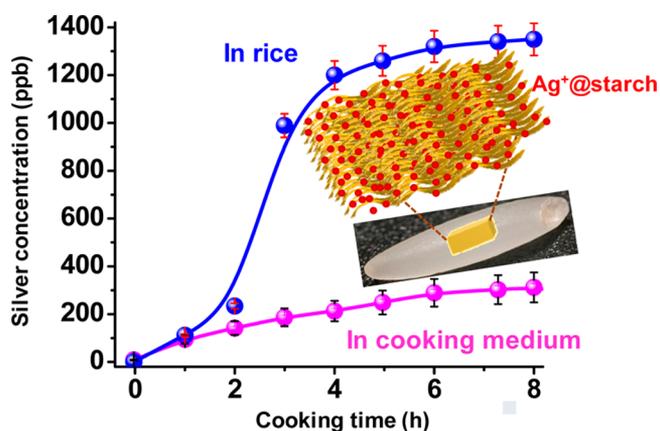


Figure 1. Concentration of silver in digested rice and in the supernatant solution (cooking medium), as a function of cooking time. The presence of silver in the polymeric starch matrix is schematically represented in the expanded inset. The error bar shows the variation of nine data points.

increase in the amount of silver in rice during cooking. Experiments were performed under various conditions to determine the most desirable consistency and softness of the cooked rice (Figures S3–S6 and experimental details given in the Supporting Information). Experiments were performed repeatedly as discussed in Methods and Experiments. Variation between the measurements was within 1%. The uptake of silver in rice and in starch solution (cooking medium) during the course of cooking shows two distinct patterns. Uptake in rice shows a rapid enhancement after an initial lag eventually reaching an equilibrium level, suggesting an equilibrium level of concentration. The extent of uptake and its kinetics depend on the rice variety. Nevertheless, rapid silver uptake while cooking after an initial lag is common in all varieties (the time-dependent uptake curves in the other rice varieties are shown in Figure S7, and the highest silver uptake by various rice varieties is compared in Figure S8) followed by a gradual saturation. As cooking progresses, the medium is gradually enriched with starch because of its dissolution in the cooking medium. As shown in Figure 1, rice shows a constant increase in silver concentration when cooked in a silver vessel with time while the concentration of silver in the supernatant reached equilibrium within a couple of hours. An \sim 5-fold increase in silver concentration in cooked rice was observed just with an increase in cooking time from 2 to 3 h. Control experiments were performed (without rice, with other parameters remaining constant), and it was seen that the concentration of silver ions released in water was lower initially (>20 ppb after 30 min) but gradually increased and reached around 170 ppb after samples had been heated for 3 h. The same finding is reflected in the uptake of silver by rice. It is proposed that silver is being released as silver ions in the solution that is taken up by rice by forming stable complexes (discussed later in the text).

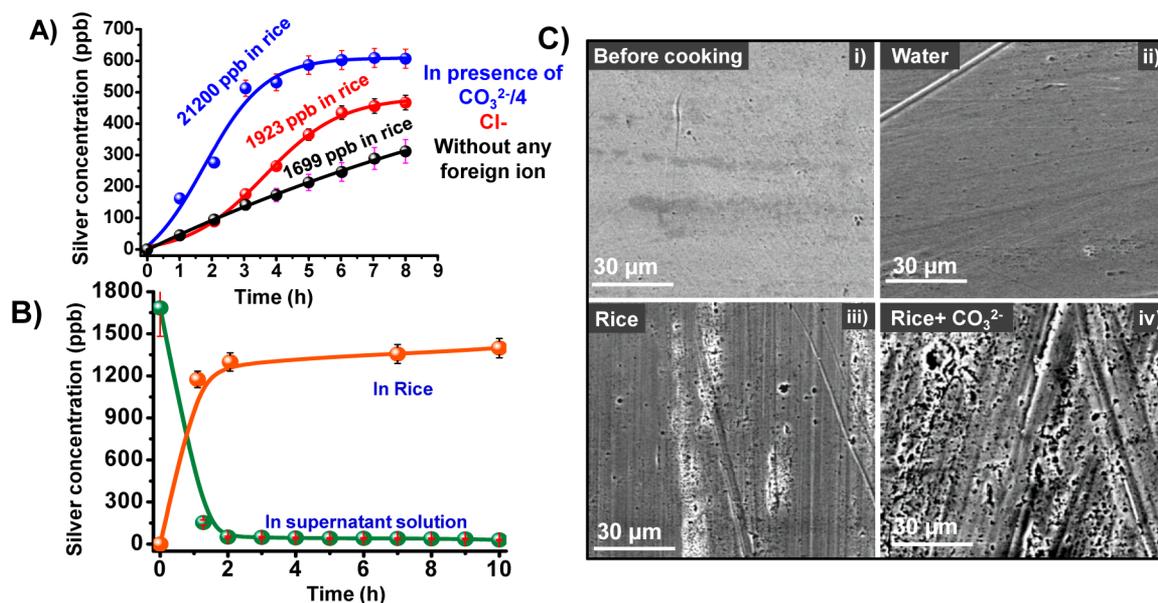


Figure 2. (A) Effect of silver ion uptake in the presence of equal concentrations of anions. CO_3^{2-} and Cl^- are compared (the cation was the same; Na_2CO_3 and NaCl were used). Corresponding concentrations of silver in cooked rice are indicated on the top of each plot. (B) Uptake of silver ions from solution when the cooking medium was 1800 ppb Ag^+ in a glass vessel. Complementary behavior was observed for the supernatant. (C) Variation in the surface morphology of silver foils due to cooking, viewed via SEM: (i) foil before the experiment and those after the experiments in (ii) DI water, (iii) rice (without any external anion), and (iv) rice in the presence of CO_3^{2-} . The error bar shows the variation of nine data points.

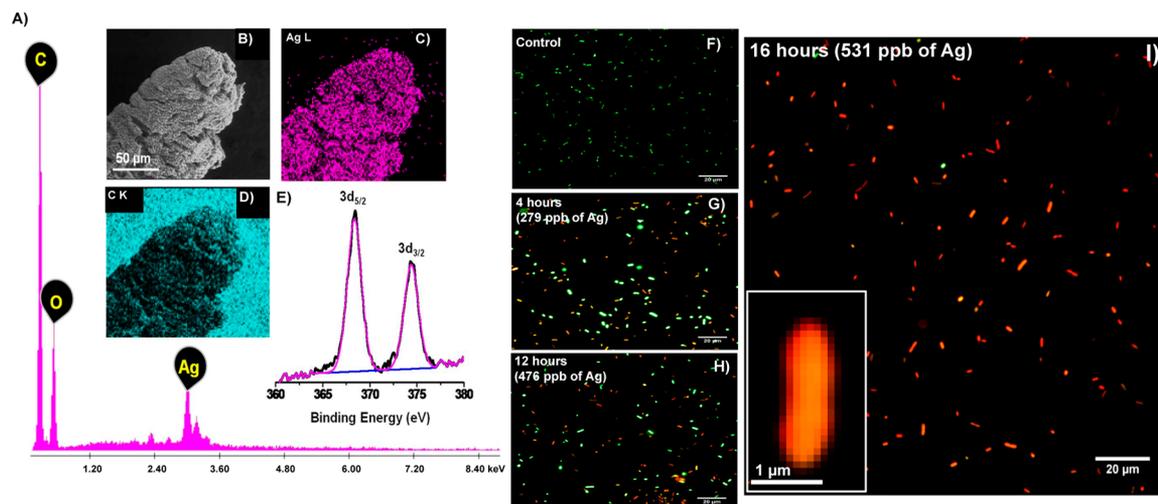


Figure 3. (A) SEM/EDS of a rice grain when it is cooked in a silver vessel showing the presence of silver. (B) SEM image of the cooked (after drying) rice. (C and D) Elemental mapping of silver and carbon. (E) Monovalent form of Ag in the rice confirmed from Ag 3d XPS. (F–I) Fluorescence images of *E. coli* MTCC 739 showing the antibacterial activity of water kept in a silver vessel. One bacterium is magnified in the inset of panel I.

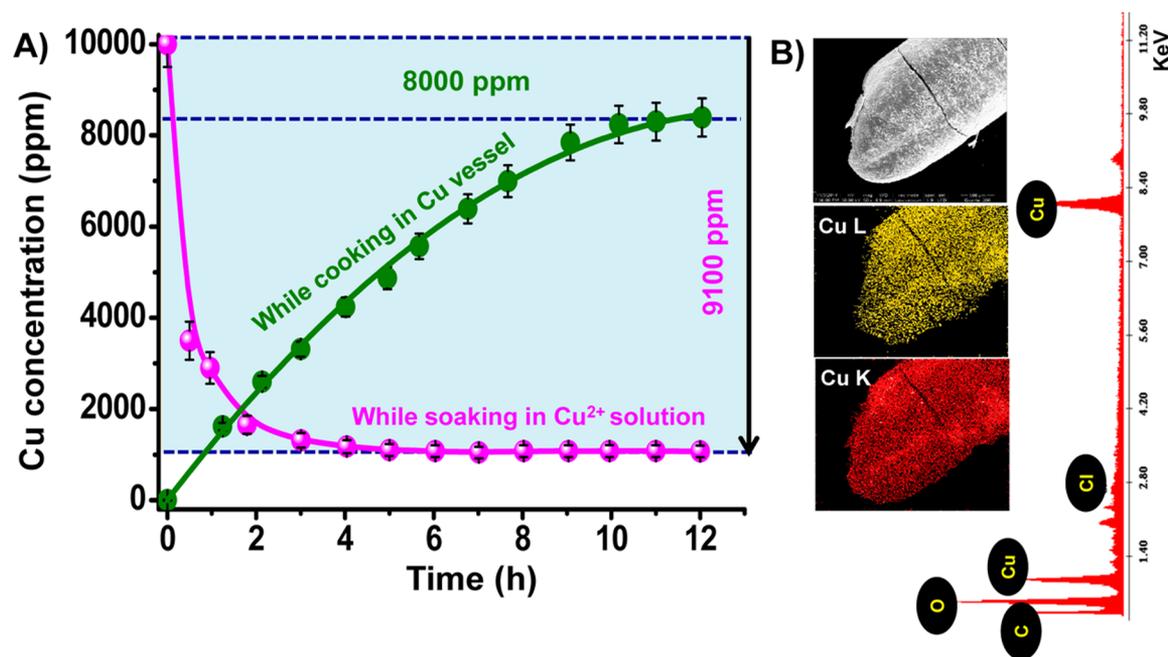
It seems plausible that silver is transported from the cooking medium (water) to rice. This conjecture was tested using various ions that can modify the silver ion concentration in solution. The ions chosen were carbonate (CO_3^{2-}), phosphate (PO_4^{3-}), and chloride (Cl^-), which are expected to form the corresponding silver species in solution, keeping the cationic (Na^+) identity unaltered (i.e., using sodium salt in each case). The solubilities of the corresponding silver salts are 0.032, 0.0065, and 0.0019 g/L for carbonate, phosphate, and chloride, respectively. Silver ion uptake in these solutions follows the general trend of solubility as stated above (Figure 2A), where data for Cl^- and CO_3^{2-} -containing solutions are compared along with the control. Phosphate follows an in-between trend.

This conclusion was further verified by cooking rice in a silver nitrate solution in a glass vessel (Figure 2B).

The uptake kinetics follow the same trend as shown in Figure 1, namely, a rapid uptake in rice and a concomitant change in solution. When silver ions are present in solution, uptake in rice is rapid. Saturated uptake can be as large as 1000 ppm when a silver salt is supplied, which makes the rice look yellow in color. The metal ion concentration in solution after cooking does not increase while the cooked rice is being cooled, implying that silver is strongly bound to the carbohydrate. The data presented show that metal ion uptake is mediated through solution. Release of silver from the vessel is manifested on the surface of the vessel in terms of corrosion. Scanning electron microscopic investigations of a polished metal surface show

Table 2. Concentrations (in parts per billion) of Metal Ions in Rice [Tamil Nadu Ponni (boiled, unpolished)] during Cooking, at Various Times When the Rice Is Cooked in a Silver Vessel

time	Cr	Mn	Fe	Co	Cu	As	Zn	Al	Ag
0 min	432.1	1454.8	3892.4	6.8	8380.8	2.3	4485.6	25.2	11.6
5 min	421.2	1423.4	3712.9	6.8	8217.8	2.3	4281.4	22.1	40.3
10 min	423.5	1435.4	3706.2	6.8	8243.7	2.1	4012.8	20.8	60.7
30 min	418.7	1385.3	3605.8	6.7	8312.5	1.9	3987.5	19.1	100.4
1 h	428.2	1312.5	2623.3	6.9	8106.9	2.1	3824.7	19.4	145.6
2 h	426.3	1276.2	2317.6	6.8	8267.0	1.9	3432.5	19.3	265.2
3 h	426.4	1206.9	2008.1	6.8	8334.4	2.3	3213.3	19.0	812.5
6 h	428.3	1109.8	1231.6	6.7	8298.4	2.2	2870.1	19.1	1384.4

**Figure 4.** (A) Concentration of Cu in rice (olive line) upon cooking in a copper vessel showing a gradual increase up to 8 h, reaching a saturation at 8000 ppm. The magenta line shows the decrease in the concentration of Cu in the solution when rice is cooked in a 10000 ppm Cu^{2+} solution in a glass vessel. (B) SEM/EDS of dried rice soaked in a 10000 ppm copper solution. Elemental maps show a uniform distribution of copper throughout the whole rice. The EDS spectrum is shown at the extreme right. The error bars show the variation of nine data points.

gradual roughening with time of cooking, which is also enhanced by the presence of other ions (Figure 2C). The rice was also cooked in a Teflon beaker in the presence of a silver foil with a 0.5 mm thickness and a 6 cm \times 6 cm area immersed in the medium. After cooking, the silver foils were washed thoroughly with DI water and dried at room temperature, and a small portion was analyzed via SEM. Highly polished silver foils were used in this study.

The presence of silver in rice was proven by several analyses as shown in Figure 3. The SEM/EDS spectrum (Figure 3A) and elemental mapping (Figure 3B–D) show a uniform distribution of silver throughout the cooked rice grain. SEM/EDS mapping of a horizontally cut rice grain is shown in Figure S9, indicating the presence of silver. This experiment confirms the uptake of silver uniformly throughout the grain. The XPS spectrum of the cooked grain in the Ag 3d region confirms the existence of monovalent silver in the grain. Ag 3d_{5/2} was observed at 367.5 eV, as expected for Ag(I).²⁹ A high silver ion concentration in the presence of carbonate and the corresponding yellowish color of rice made us consider the possibility of formation of silver nanoparticles within rice. Metallic silver nanoparticles have strong absorption at 400 nm

known as a plasmon band.³⁰ The peak position varies slightly depending on the protecting ligand. However, there was no plasmonic feature in the UV–vis absorption spectrum of the same sample (Figure S10). This confirms that silver nanoparticles were not formed in rice while it was being cooked. This aspect was studied as carbohydrates can reduce silver to form silver nanoparticles, which is more facile in the presence of ions like carbonate. LDI MS of silver-saturated rice was performed, and small silver clusters were detected (Figure S11). However, a similar kind of mass spectrum can be obtained by LDI of Ag salts, too, as Ag⁺ ions can form aggregates in the gas phase during laser ablation.^{31,32}

Release of Ag ions into the solution from the metal can occur in water under experimental conditions (i.e., at 80 °C). In DI water with a conductivity of 0.7 μS , silver release is up to 531 ppb at 80 °C, for a 16 h incubation. This follows a constant increase up to 16 h, which was monitored up to 24 h (Figure S11). Such a silver ion concentration is enough to cause biological activity as seen by live and dead staining of *E. coli* as shown in Figure 3I (all the antibacterial experiments were conducted at room temperature after the water had been cooled). Live and dead staining was used to see this effect (see

Antibacterial Test for details). The fraction of live bacteria (green) decreases with an increasing contact time of the sample (Figure 3G,H), and there were no live bacteria (all are red) after a 3 h exposure to silver-containing water. The concentration of silver was 531 ppb at this time (heating for 16 h). One of the dead bacterium is magnified in the inset of Figure 3I.

The data suggest that silver ions are complexed strongly with starch, although it was not possible to identify the chemical identity of the complex thus formed. In view of this, we examined the interaction of glucose (the composing unit of starch molecule) with silver in aqueous solution, using ESI MS. Ag–glucose complexes are known to form in solution and can be seen via ESI MS analysis. Boutreau et al. have shown that the α -anomer of glucose can effectively form complexes with silver through the -OH groups at positions 3 and 4.³³ Peaks at m/z 287, 367, etc., corresponding to G–Ag⁺, 2G–Ag⁺, etc., complexes, respectively were observed via ESI MS in positive ion mode. The species was confirmed by isotope distribution as well as ESI MS/MS studies. Glucose aggregates also show similar kinds of complexes in the gas phase (see Figure S12A). Sucrose (disaccharide composed of glucose and fructose) also forms complexes with silver (see Figure S12B). Therefore, we can conclude that polysaccharides like starch can also form complexes with silver.

Experiments were also performed with polished and unpolished varieties of the same rice and showed that the latter take up more silver than the former (for the same rice variety). Thus, the bran layer appears to be the principal site of silver uptake from the cooking medium (Figures S7 and S8).

To understand whether silver is exchanging with other metal ions, careful examination of the concentration of other essential metal ions was performed. ICP MS data of different metal ions in cooked rice prepared in silver vessels are listed in Table 2. The data suggest a considerable decrease in the concentration of Fe and Zn in rice when it is cooked in a silver vessel. This observation suggests the substitution of these binding sites by silver. In this case, rice was cooked in three different vessels (as discussed in Methods and Experiments), and it was analyzed after specific time intervals. Seven different sets of experiments were performed using 2 g of dry rice and 20 mL of DI water.

The uptake of copper and aluminum during cooking in respective vessels was also studied. The optimized cooking procedure described above was followed. In the case of a copper vessel, uptake of up to 8000 ppm was observed. As seen with silver, a gradual increase in copper concentration in the cooked rice was observed. When the rice was cooked with DI water containing 10000 ppm of Cu²⁺ in a glass vessel, a gradual decrease in Cu²⁺ concentration was seen in the supernatant. Approximately 900 ppm of Cu was observed in the supernatant, and rice contained 9100 ppm (magenta line in Figure 4A). The presence of Cu was further proven via SEM/EDS analysis of the dried rice sample. A uniform distribution of Cu was observed in the rice (see Figure 4B).

The uptake of metal was the lowest upon cooking in an aluminum vessel, compared to those in silver and copper vessels. The extent of uptake reached a maximum of 580 ppb for Al after 2 h of cooking, which declined to 100 ppb after 6 h, but the uptake was far higher when the rice was soaked in Al³⁺-containing water, where ~5000 ppb of Al was found in the cooked rice after 6 h of cooking. The lower solubility of Al salts in water is likely the cause of the lower uptake during cooking in aluminum vessels. Furthermore, the binding of starch to Al is

likely to be weaker than that to Cu and Ag, accounting for lower uptake. In addition, the protective layer of oxide on the aluminum vessel surface may retard corrosion and consequently slow the release of Al into the solution. Here a dried rice sample also showed a uniform distribution of Al in SEM/EDS (Figure S13).

CONCLUSION

Our study probed the biomolecule-induced corrosion of metal surfaces during cooking, leading to unprecedented uptake of metal ions in foodstuffs, leading to a potential impact on human health. Metals such as silver, copper, and aluminum are taken up by rice from the cooking vessels made of the respective metals, and this leads to microscopic corrosion of the vessels. Uptake occurs via solution by the formation of soluble ionic species of the metals. The presence of anions in solution, whose metal salt is water-soluble, enhances the metal ion uptake. Uptake is enhanced by the presence of bran. Ag uptake happens with a corresponding decrease in the Fe and Zn concentration in rice, suggesting a substitution mechanism for metal ion uptake. The uptake of metals by rice from utensils occurs principally through the ionic route. Cooking methods enhance the release of ions into the medium, such as the use of acids, salts, and complexation agents that can have much stronger effects.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b00980.

Additional details describing the experimental details, SEM images of different vessels before use, initial concentrations of different metal ions in water, release of silver in deionized water, temperature-dependent release of silver, time-dependent release of silver at 80 °C in DI water, pH-dependent release of silver, time-dependent silver uptake by different rice varieties, maximal silver uptake by different rice varieties, SEM/EDS of cooked rice horizontally cut with adsorbed silver, UV–vis spectra of the supernatant solution, LDI MS of silver-saturated rice, ESI MS of Ag–glucose and Ag–sucrose complexes, and SEM/EDS of cooked rice soaked in an aluminum salt solution (PDF)

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Notes

The authors declare no competing financial interest.

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