

Sparingly Soluble Constant Carbonate Releasing Inert Monolith for Enhancement of Antimicrobial Silver Action and Sustainable Utilization

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Supporting Information

ABSTRACT: Silver, a metal with phenomenal commercial importance has been exploited in its ionic form in the field of water purification, with the objective of delivering microbially safe drinking water. Silver released at such concentrations is unrecoverable and has to be reduced to ensure sustainable utilization of the metal. We have shown that small concentrations of carbonate can effectively bring down the amount of silver ion used for microbial disinfection by half. Implementation of this finding requires constant carbonate releasing materials in natural water for an extended period. In this work, we describe a hybrid material with intrinsically high stability in water that is prepared using naturally abundant ingredients which releases carbonate constantly and in a controlled fashion. This composition in conjunction with reduced silver ion concentration delivers mircobially safe water, tested with *E. coli* and MS2 phage. Use of constant carbonate releasing materials in the anterial for antimicrobial applications can reduce the unrecoverable silver released into the



environment by ~1300 tons/year. We also show that the composition can be modified to release cations of choice without disturbing the CO_3^{2-} release from the same. A sustained release of selective cations along with carbonate can supplement drinking water with the minerals of interest.

KEYWORDS: Carbonate materials, Sustainable release, Synergetic effect on silver, Enhanced antimicrobial activity, Drinking water purification

INTRODUCTION

Silver in its ionic form has been a subject of numerous investigations and is commercially exploited for its antimicrobial activity in drinking water purification.¹ Nevertheless, delivering silver ions at sustained concentrations of relevance to achieve antimicrobial activity has been a challenging task. Numerous approaches are available for the synthesis of biocidal silver nanoparticles or colloids using matrices.² The biocidal property of silver nanoparticles is attributed to the release of trace quantities of silver ions in water.^{2d,e} Antibacterial effect of transition metals, including silver, is usually named as oligodynamic effect, as it is most effective at low concentrations due to the solubility limits imposed by various anions. Due to this reason, they cannot exist as free ions at higher concentrations in real water.^{2f} It is also appropriate to reduce the consumption of silver in view of the potential risks to both primitive and developed organisms.^{2e} Although nanoparticles release silver ions more efficiently than the bulk metal, massive deployment of such products has been hampered due to the following reasons: (a) drinking water contains many species (e.g., inorganic ions and organics) that anchor on the surface of the nanoparticles, making the release of sustained silver ions difficult;³ and (b) surface fouling due to silicates present in water retards Ag^+ release consequently quenching the antimicrobial activity. Therefore, a sustainable solution for safe drinking water is an important aspect.⁴

Introduction of novel nanostructures with constant and controlled silver ion releasing capability is proposed to be a remedial method.⁵ However, the free silver ion concentration available for antimicrobial activity depends on the water chemistry, especially the presence of various anions.⁶ For a specific silver ion concentration, the antimicrobial performance is in the order, seawater \leq high organic matter-containing water \leq high divalent cation-containing water \leq synthetic water, due to the speciation of Ag^{+,7} In this aspect, we have found that one of the anions, namely carbonate (CO_3^{2-}) can effectively enhance the antimicrobial activity of Ag⁺ reducing the overall annual global silver requirement used for antimicrobial applications by half, i.e., to the extent of ~ 1300 tons.⁶ This anion factor enhancing the sustainable utilization of noble metals can be industrially utilized only with the development of sustainable CO₃²⁻ releasing materials at desired concentrations.

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Figure 1. Schematic representation of the synthesis of carbonate releasing monolith $(C_{CO3}/C_{CO3/K})$ and a water purification system based on the same. The products are solid rock-like substances, in the shape of the mold which may be crushed or used as such.

However, requirement of precise carbonate concentrations and consequent need of trained manpower to maintain the carbonate ion concentration in the water purification plant are limiting the field-deployment of this technology. The release rate of highly alkaline carbonate ions in the treated water should be constant and controlled to maintain the pH of drinking water. Also, the release rate of carbonate ions from the corresponding salts regulate the time period of utilization of carbonate salts in continuous flow of water. In addition, sustained carbonate release must occur along with silver for delivering bacteria and virus-free safe drinking water. In this context, no commercially available sustained carbonate ion releasing products for drinking water purification are available until now. Essential inorganic minerals like calcium, magnesium, sodium, potassium, iron, and zinc, which occur at milligram per kilogram quantities in the body, are crucial for the human system. "Water" can serve as a source of these essential ions to meet the body's mineral requirement.⁸ In this study, we also show that the sustained release formulation can be modified to release the mineral ion of interest through drinking water based on the deficiency present at a given source.

In this paper, we introduce a new composition for this purpose which releases CO_3^{2-} at the required concentration of 20 ± 5 ppm at ambient temperatures. It contributes to the sustainable utilization of resources, yet efficiently delivering cent percent safe potable water solving one of the important problems of humanity.⁹ Dissolution of sparingly soluble salts has also been a part of interest in the context of measuring volume of water passed through a device, and also in terms of pH control.¹⁰ However, none of these reports is concerned with the release of CO_3^{2-} ions, especially for effectively enhancing the antimicrobial activity.

Although most of the surface waters and ground waters contain sufficiently high concentration of carbonates and bicarbonates (>180 ppm), this hard water is undesirable for drinking. In most cases, hardness is removed which removes the carbonates too. At a higher pH, after reaching a supersaturation point (pH: 7.5-8.0, alkalinity: 80-160 ppm, and saturation index: 1.5) these carbonates precipitate forming turbid water. But, carbonate concentration released from the

designed material is constantly maintained at 20 \pm 5 ppm, which is below the required saturation index and alkalinity due to which precipitation of CaCO₃ does not occur.

In an attempt to create a stable structure, releasing carbonate, various template forming precursors were used to embed carbonates. Due to the requirement of chemical inertness and structural integrity in water as mentioned before, silica and alumina were our natural choices for forming templates. A stable composite of silica with enhanced robustness at a temperature below the melting point of CO_3^{2-} was achieved by optimizing several combinations of silica and carbonates. The addition of different forms of carbonates acted as a flux material in reducing the melting point of silica. Each of the compositions prepared were analyzed for the release characteristics and the optimized compositions were arrived at. A trace amount of 4.3% of alumina was used to strengthen the mechanical properties of silica scaffold. Al₂O₃ has high bioinertness,¹¹ high abrasion resistance, and high hardness, all of which make it suitable as a material of use in water.¹² In the template, the carbonates were trapped within the porous silica cages. The pores are small enough allowing CO_3^{2-} to be preserved with reduced, yet sufficient, interaction with water, due to which the release of CO_3^{2-} is constantly maintained in the range of ~20 \pm 5 ppm. This uniformity and reduced release rate at an immersed condition are difficult to achieve in a carbonate releasing material. The monolith prepared works as a controlled anion releasing system maintaining an equilibrium concentration above which further release does not occur. We also show that the designed monolith can be modified to release other ions of interest and it is demonstrated here for potassium release, without disturbing the release of carbonate.

EXPERIMENTAL SECTION

The carbonate releasing monolith was synthesized using a solid state route. It was made by melting silica and traces of alumina at the lowest possible temperature such that carbonate does not decompose into the corresponding oxide and carbon dioxide.¹³ The mineral cristobalite is a high-temperature polymorph of silica seen at equilibrium formation temperature of 1470 °C at atmospheric pressure. Moganite is a silicate mineral, considered as a polymorph of quartz formed at 1354 °C. The composition of the raw materials was optimized in such a fashion that

the cristobalite and moganite matrices can be formed at temperatures below the melting point of carbonate (850 $^{\circ}$ C). Inclusion of carbonates was not only considered as an anion for release but also as a flux, reducing the melting point of silica.

All the chemicals used were purchased from Sigma-Aldrich and used as such. Unless otherwise specified, all the reagents used were of analytical grade. Our objective was to create a template in which carbonate releasing components can be held strongly at the largest extent, along with controlled release. Various optimization studies were undertaken to ensure that the scaffold created holds carbonate, ensuring constant release.

Synthesis of Sustained Carbonate Releasing Materials, C_{CO3} . The carbonate releasing composite, abbreviated as C_{CO3} , comprising of a porous scaffold was loaded with the source of carbonate namely, sodium and potassium carbonates. Figure 1A describes a schematic outline of the synthesis of C_{CO3} and a water purification method based on the same. The mixture of SiO₂ and Al₂O₃ as raw materials for scaffold and the anion sources, namely Na₂CO₃ and K₂CO₃ (in the ratio of 74.1:4.3:16.8:4.75 by wt%, respectively), were homogenized and packed in molds and sintered at 800 °C for 1 h. Decomposition temperatures of Na₂CO₃ and K₂CO₃ are 858 and 898 °C, respectively, at atmospheric pressure.¹⁴ The composite material formed was cooled to room temperature followed by washing with water at ambient condition, which was used for further experiments.

Synthesis of the Material for Sustained Release of Carbonate and Potassium lons, $C_{CO3/K}$. The synthesis of potassium and carbonate releasing composite, abbreviated as $C_{CO3/K}$, involves a mixture of SiO₂ and Al₂O₃ as raw materials for the scaffold composition; Na₂CO₃, CaCO₃, and K₂CO₃ as sources of anions; and K₂CO₃ and KCl as sources of potassium (with SiO₂:Al₂O₃:Na₂CO₃:K₂CO₃:CaCO₃:KCl in the ratio, 40.6:2.4:31.5:7.6:12.0:6.0 by wt%, respectively). These raw materials were homogenized, packed in molds, and sintered at 850 °C for 1 h. The C_{CO3/K} composite material formed was cooled to room temperature followed by washing with water at ambient condition and was used for further experiments.

Kinetics of Sustained Release of Carbonate. Batch Mode. The kinetics of carbonate release from the material was studied using the following experimental procedure. Ten milligrams of the carbonate incorporated pellet granulated as ~72 μ m particles was shaken briefly in 10 mL of Milli-Q water. Carbonate concentration released in the test water at different contact times was calculated based on the quantification of total inorganic carbon, measured at each step using a total organic carbon (TOC) analyzer (Shimadzu TOC-V_{CPH} model). The instrument was calibrated earlier using anhydrous sodium carbonate and anhydrous sodium hydrogen carbonate. The TOC measurements were performed using Millipore water whose inorganic carbon content was monitored for every individual experiment and considered as a blank.

Cartridge Mode. The performance of the material under continuous flow of water was tested in the cartridge mode. A cartridge containing 1 L of tap water was treated with 1 g of the material, C_{CO3}. After 15 min of standing time, the total dissolved solids (TDS), expressed in terms of electrical conductivity (μ S/cm), and the change in pH of the water were measured as indications of carbonate released into the water. The cartridge was drained and filled with a fresh batch of tap water (1L) and the above procedure was repeated to monitor the release. This cycle was repeated until all the CO₃^{2–} present in the material was exhausted. The material, C_{CO3} ran up to 50 L of water (50 cycles) after which no change in pH or TDS was observed. After every 10 cycles of the above procedure, the material was dried for 18–20 h at room temperature and was tested for further CO₃^{2–} release.

Biocidal Enhancement Property of the Material. Enhancement in the biocidal property of Ag⁺ was measured by spiking 100 mL of the natural drinking water with Ag⁺ (40 ppb) and Ag⁺ (40 ppb)/CO₃²⁻ (15–20 ppm released from 100 mg C_{CO3}). In case of antibacterial activity, *Escherichia coli* (*E. coli* ATCC 25922) at a concentration of ~1 × 10⁵ CFU/mL was spiked, whereas antiviral activity was measured by spiking the water with bacteriophage, MS2 (ATCC 15597-B1) at a concentration of ~1 × 10³ PFU/mL.

Thereafter, the water was left to stand for 1 h and subsequently the surviving microorganism count was measured by conventional pour plate (*E. coli*) and plaque assay (bacteriophage MS2) techniques. Colony counts were performed after incubation at 37 $^{\circ}$ C for 48 h (*E. coli*) and 16 h (bacteriophage MS2).

The designed water purification device, schematically described in Figure 1B, was anchored along with the Ag^+ releasing material from our previous work⁵ packed in a cartridge form, before the carbonate releasing system. Dissolution of silver ion in the presence of various anions was reported from our group.¹⁵ The data revealed that the leaching of Ag^+ from silver foil can be reduced to half (from 140 to 66 ppb) when immersed in distilled water spiked with carbonate (up to 50 ppm). Thus, the carbonate releasing monolith was placed above the Ag^+ releasing system which spontaneously reduces the silver ion release into the water flow. This system results in complete and enhanced biocidal activity on *E. coli* and bacteriophage MS2, the surrogates for water borne pathogens (bacteria and viruses, respectively). The removal of the microbial debris by a filter connected to an output delivers pure drinking water.

Characterization Techniques. Morphological studies of the carbonate releasing monolith, elemental analysis and elemental mapping were carried out using a scanning electron microscope (SEM) equipped with energy dispersive spectroscopy (EDS) (FEI Quanta 200). X-ray photoelectron spectroscopy (XPS) measurements were performed using an ESCA Probe TPD of Omicron Nanotechnology with the polychromatic Mg K α as the X-ray source (hv = 1253.6 eV) and the binding energy was calibrated with respect to C1s at 284.5 eV. The release of aluminum, calcium, sodium, and potassium concentrations in the water were estimated using inductively coupled plasma spectroscopy (ICP-MS) (PerkinElmer Nex ION 300 ICP-MS). Carbonate concentration was calculated based on the quantification of total inorganic carbon present in the test water using Shimadzu TOC-V_{CPH}. Raman spectra were obtained with a WITec GmbH, Alpha-SNOM alpha 300 S confocal Raman microscope having a 532 nm laser as the excitation source.

RESULTS AND DISCUSSION

Characterization of the Sustained Carbonate (C_{CO3}) and Potassium (C_{CO3/K}) Releasing Materials. The SEM image of the granular particles of the monolith and their chemical compositions are shown in Figure 2. The granules (40–100 μ m) of C_{CO3} confirms the porous (see the arrows) but crystalline morphology shown in Figure 2A. The patterns around the particles are due to the carbon substrate used for mounting the material. Porosity is evident in Figure 2B too, the inset of which illustrates the Raman spectrum; the strongest band at 1057 cm⁻¹ is the symmetric stretching mode (v_1) of the carbonate ion.¹⁶ The weak band at 1076 cm⁻¹ of the cristobalite phase¹⁷ might be buried under the high intensity of carbonate stretching. Figure 2C shows the corresponding energy dispersive X-ray spectrum (EDS) which confirms the presence of carbon, oxygen, silicon, potassium, and sodium. Insets show the elemental mapping of a single grain of the material.

Initial components and the designed carbonate releasing composite material were studied by XPS. Figure 3A shows the survey spectra and Figure 3B depicts the deconvoluted C1s XPS spectra showing adventitious carbon at 284.6 eV¹⁸ and carbonate at 289.3 eV¹⁹ and potassium $K2p_{3/2}$ at 293.0 eV (and $K2p_{1/2}$ at 295.8 eV).¹⁹ This clearly indicates that carbonate and a small portion of potassium are entangled in the SiO₂ matrix. The deconvoluted spectra shown in Figure 3C confirms the presence of oxygen, where O1s peaks appear in the range of 531.5–532.0 eV for metal carbonates and 532–533 eV for SiO₂.

Figure 3D shows the X-ray diffraction pattern of the amended granular composite before and after heating. Initially,



Figure 2. (A and B) SEM images of 72 μ m granules of the monolith loaded with carbonate (C_{CO3}). The image in panel B shows the porous surface of a granule with the inset representing Raman feature specific for carbonate. (C) A corresponding energy dispersive X-ray spectrum (EDS) along with the elemental maps.



Figure 3. (A) X-ray photoelectron spectra of the carbonate releasing monolith (C_{CO3}) before and after heating. (B and C) show the deconvoluted XPS spectra of corresponding C1s and O1s regions, respectively. (D) Powder XRD patterns of the material before heating and after heating. The material C_{CO3} formed after heating (i) is compared with the (ii) cristobalite phase of SiO₂ [JCPDS 39-1425]. The composition mixture (iii) before heating is compared with (iv) monoclinic phases of K_2CO_3 [JCPDS 16-820] and (v) Na₂CO₃ [JCPDS 19-1130]) as well as the (vi) tetragonal phase of SiO₂ [JCPDS 15-0026].

tetragonal phase of SiO₂ (JCPDS 15-0026) and monoclinic phases of K₂CO₃ [JCPDS 16-820] and Na₂CO₃ [JCPDS 19-1130] were the principal components of the precursor of C_{CO3}. Upon heating, the XRD pattern shows peaks at 2θ (degree) at 22.00, 28.47, 31.49, 36.13, 36.41, 47.10, and 48.65 which correspond to (101), (111), (102), (200), (112), (113), and

(212) planes of cristobalite. Despite the dominating cristobalite phase, the matrix contains 21.5 wt% of sodium and potassium carbonates which may be present in an amorphous form. From the release data presented, we understand that $CO_3^{2^-}$ is continuously leached retaining the framework. Total released $CO_3^{2^-}$ amounts to 20 wt% of the monolith confirming the nearly complete retention of $CO_3^{2^-}$ in the prepared structure. To the best of our understanding, anion releasing compositions of this kind are unknown. It appears that a small fraction of carbonate has decomposed releasing CO_2 , explaining the porous structure and the slightly reduced reduction in the extent of carbonate released.

The sustained carbonate and potassium ion releasing material $(C_{CO3/K})$ is a formulation modified to release the ion of interest, demonstrated here for potassium. Figure S1A shows the SEM image of the monolith, C_{CO3/K}. The image in panel B shows the porous surface of the grain with the inset representing the Raman spectrum; the strongest band at 1062 cm^{-1} which is the symmetric stretching mode of the carbonate ion.¹⁶ Shift in the stretching mode from 1057 to 1062 cm^{-1} is due to the influence of potassium and other ions. Figure S1C shows the corresponding EDS which confirms the presence of carbon, oxygen, silicon, potassium, calcium, and sodium. Insets show the elemental mapping of a single granule of the material impregnated with CO_3^{2-} and K⁺. Figure S2 shows the XPS of the initial components and the monolith, C_{CO3/K}. Figure S2A illustrates the survey spectra and Figure S2B is the deconvoluted C1s XPS spectra showing the presence of C-C at 284.9 eV due to the adventitious carbon¹⁸ and the carbonate peak at 289.9 eV.¹⁹ The presence of potassium is shown by K2p doublet at 293.0 eV $(K2p_{3/2})$ and 295.2 eV $(K2p_{1/2})$.¹⁹ This clearly indicates that carbonate and a greater portion of potassium are entangled in the SiO₂ matrix. It is further confirmed from the deconvoluted O1s spectra, as shown in Figure S2C where the peaks appear in the range of 531–533 eV for metal carbonates and SiO₂, respectively. Figure S2D shows the X-ray diffraction pattern of C_{CO3/K} before and after heating. The tetragonal phase of SiO₂ [JCPDS 15-0026] and monoclinic phases of K₂CO₃ [JCPDS 16-820] and Na₂CO₃ [JCPDS 19-1130] are dominant in the precursor material as noted before. Upon heating, the SiO₂ has changed into a silicate mineral, moganite [JCPDS 38-360], whereas K₂CO₃ and Na₂CO₃ were changed to the potassium sodium carbonate [JCPDS 1-1038]. This clearly reveals that moganite acts as the matrix resulting in the monolith. From the anion and cation release data to be presented below, we understand that CO_3^{2-} as well as the cation of interest are continuously leached retaining the framework.

Kinetics of Carbonate Release from the Material. The concentration of CO_3^{2-} leached into drinking water from the prepared monolith is highly tunable at relevant temperatures (5–35 °C) and varying TDS (100–1000 μ S). The carbonate release does not alter the pH of the water beyond the permissible limit of 6.5–8.5.^{5,6} The release occurs within 5–15 min of contact time and concentration of the release does not exceed 20 ± 5 ppm even when there is a prolonged contact time tested up to 12 h in batch mode (Figure 4A). Figure 4A (inset) describes the release of carbonate in a sustained fashion under a continuous flow of 50 L water in cartridge mode. The material was tested using tap water in the cartridge mode, where the performance was not affected by the deposition or interference of other ionic species present in the test water. After every 10 cycles of exposure to water, the material was



Figure 4. Kinetics of carbonate release from the monolith (C_{CO3}) for prolonged period of exposure to water. Inset shows the sustained release of carbonate in continuous flow of water (A). Carbonate-supported antibacterial activity of 50 ppb silver (B) and 1 ppm zinc and 500 ppb copper (C). Carbonate-supported antiviral activity of 50 ppb silver, 1 ppm zinc, and 500 ppb copper (D).

drained and dried for 18-20 h at room temperature and was tested for further CO_3^{2-} release. After every step of drying of the sample, an increased release of CO_3^{2-} in the first 15 min of exposure was observed (shown as a spike in the graph at trial numbers 11, 21, and 31). These spikes are attributed to the prolonged soaking of the material by the stagnant water clogged within the pores during the slower rate of drying at room temperature. The dissolved carbonate inside the pore is released faster when the material is soaked in a fresh batch of water. It is not of consequence to the water purification device as the initial water collected is often discarded in typical use.

The synthesized monolith initially consisted of 21.5% CO₃²⁻ (as sodium and potassium carbonate) by weight and upon passage of 50 L of water it leached 20 wt% of material. The amount of CO₃²⁻ leaching was reduced slowly with increasing number of trials (observed after the passage of 35 L). Theoretically, leaching of 20 wt% CO₃²⁻ amounts to an average concentration of 20 ppm over passage of 50 L, using 1 g of the monolith. The tests were stopped after 50 trials as the material had released nearly all the entrapped CO₃²⁻.

The carbonate is an integral part of the composition itself and thus, reloading the cristobalite or moganite monolith with carbonate, although conceivable, has not been attempted in this study. The loaded carbonate, if not an integral part of the composition, will dissolve completely in water delivering undesirable pH and taste. It is for this reason, an inexpensive and environmental friendly scaffold material (silica) was chosen.

Biocidal Enhancement Property of the Material. The monolith, C_{CO3} , was tested for enhanced antibacterial activity in batch mode (Materials and Methods) for released carbonate on 50 ppb Ag⁺ (Figure 4B), 1 ppm Zn²⁺, and 500 ppb Cu²⁺ (Figure 4C) in natural drinking water. The minimum concentration of the individual metal ion, required to achieve antimicrobial activity was chosen. Enhancement in the bactericidal activity was observed in water pretreated with the

material releasing CO_3^{2-} (Figure 4D). Effect of the eluted CO_3^{2-} on virus surrogate MS2 bacteriophage treated with Ag⁺ was tested. We observed that while 50 ppb Ag⁺ alone (even after 1 h contact) was unable to affect the phage, the combination of 50 ppb Ag^+ added to water pretreated with the material releasing CO_3^{2-} , was found to achieve effective antiviral property within a contact time of 15 min. Therefore, we show that 50 ppb of Ag⁺, not only acts as an antibacterial agent but also as an antiviral agent in the presence of carbonate. This property is not observed otherwise in this limited range of silver ion concentration (20-50 ppb). Similarly, the synergic effect of C_{CO3} on other metal ions, like Zn^{2+} and Cu^{2+} (1 ppm and 500 ppb, respectively), was also demonstrated. The enhanced effect due to carbonate is because of the interactions with the peripheral proteins of the bacterial membrane.⁶ These peripheral proteins are associated with the membrane lipids and other proteins via electrostatic forces or hydrophobic interactions. Thus, conditions like high salt concentrations or an alkaline environment disrupt the interactions leading to the detachment of peripheral proteins. Therefore, in the presence of CO_3^{2-} , a disturbed membrane, free of peripheral proteins is suspected, which allows the penetration/cellular mobility of Ag⁺, by increasing the bioavailability of silver ions.

In an attempt to modify the property of the composite to release other ions, we found that this material can be generalized for the release of not only anions but also cations, illustrated here using potassium. K⁺ is an essential element for human nutrition and the requirements are generally measured in grams per day.²⁰ Potassium and sodium maintain normal osmotic pressure in cells and help the muscles to contract.²¹ It is a cofactor for many enzymes and is required for the secretion of insulin, creatine phosphorylation, carbohydrate metabolism, and protein synthesis.²² The release of K⁺ in water was therefore tuned in a controlled fashion and this modification did not affect the sustained CO₃²⁻ releasing property of the material. Similar to C_{CO3}, the C_{CO3/K} showed a release of CO₃²⁻

within 5-15 min of contact time and concentration of release was within 20 ± 5 ppm in batch mode (Figure S3A). Inset in Figure S3A describes the release of carbonate from the cartridge device containing 1g of the pellet. The material, C_{CO3/K} did not release any other ion in significant quantities from its framework during interaction with water. Figure S3B demonstrates the selective release of potassium and sodium while release of other undesirable cations is controlled from C_{CO3/K}, when immersed in water. Figure S3C displays the synergetic effect toward the antibacterial activity by the steadily released carbonate ion (from $C_{CO3/K}$), with various metal ions (50 ppb Ag⁺, 1 ppm Zn²⁺, and 500 ppb Cu^{2+}) in batch mode. The reduction of bacteria and virus count at a faster rate clearly indicates the effective synergy between the released carbonate with the metal ions used for water purification $(Ag^+ \text{ or } Cu^{2+} \text{ or }$ Zn^{2+}). Further, the sustained release of potassium from $C_{CO3/K}$ does not alter the biocidal activity of the present system. A possible mechanism for enhanced biocidal activity of Ag⁺ due to carbonate has been discussed in our previous work.

Silver in the ionic form continued to be available during the period of antimicrobial activity in the conditions of test water. This was verified by measuring Ag^+ concentration at varying time intervals using ICP MS (Figure S4).

We report a composite, forming a structurally stable monolith, releasing carbonate ion in water at a fixed concentration for a prolonged period to enhance the antimicrobial property of silver ion. We have achieved the formation of robust matrices of cristobalite and moganite at temperatures below their standard formation temperatures, which entrap anions and cations of interest. The monolith has been prepared with inert template forming materials and it releases carbonate ion at 20 ppm concentration, which does not change even upon longer periods of exposure to water at room temperature. This carbonate concentration brings down the requirement of Ag⁺ for effective antimicrobial activity in water purification applications, reducing the global unrecoverable loss of silver by \sim 1300 tons per year. Besides, the proposed material acts as a system for enhancement of the biocidal activity of metal ions in general. This material can be used along with several water purification technologies especially reverse osmosis, ultraviolet irradiation, ozonation, adsorption, and membrane filtration techniques as a synergetic enhancement system delivering complete biocidal activity in potable water.

Other ions such as potassium may also be released controllably so that "enhanced" water may be supplied. Various modifications of the designed monolith with different compositions can be developed for additional release of both anions and cations, with comparable performances.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acssuschemeng.6b00979.

Scanning electron microscopic images, energy dispersive X-ray spectrum with elemental mapping, Raman spectrum, and XRD and XPS of the sustained carbonate and potassium releasing material ($C_{CO3/K}$). Kinetics of carbonate release and potassium release from $C_{CO3/K}$ for prolonged period of exposure to water and carbonate-

supported antimicrobial activity of Ag^+ , Zn^{2+} and Cu^{2+} (PDF)

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Notes

The authors declare no competing financial interest.

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