RESEARCH PAPER

Efficiency of Cu, Ag, and Fe Nanoparticles as the Detergent Preservatives Against *E. coli* and *S. aureus*

Marzieh Miranzadeh[1], Mohammad Zaman Kassaee[1*], Fahimeh Afshari[2]

[1] Department of Chemistry, Tarbiat Modares University, Tehran, Iran

[2] Industrial paints of Iran Co., Isfahan, Iran

ARTICLE INFO

ABSTRACT

In this study, Cu, Ag, and Fe nanoparticles (NPs) are used in shampoo, hand washing liquid (HWL) and dish washing liquid (DWL) instead of the conventional synthetic preservatives such as isothiazolinones; since the latter often act as potent sensitizers leading to development of allergic contact dermatitis. The above NPs are considerably effective against *Escherichia coli* and *Staphylococcus aureus*. Our metal NPs are deliberately made durable and pure through arc fabrication. They appear in spherical morphology as indicated by XRD and SEM. The shampoo formulation with 0.1 g/L Cu NPs and HWL and DWL with 0.1 g/L Ag NPs exhibit the best antibacterial activity against tested *E. coli* and *S. aureus*. Generally, the order of antibacterial activity of these preservatives is: Cu NPs>Ag NPs> Fe NPs.

How to cite this article

INTRODUCTION

A detergent, as a kind of synthetic surfactant, is engineered to perform under desired conditions [1] and composed of water, primary surfactant (cleansing agents), foam boaster, thickeners, modifiers, and desired additives [2-6]. While, the sterility of detergents is not often necessary, contamination with pathogenic microorganisms and microbial contaminants, especially in high numbers, are not desired [7]. In addition, transmission of bacteria on the skin can cause infections [1]. Microorganisms such as *E. coli*, *S. aureus*, and *P. aeruginosa* easily grow in places not completely dried up (bathtubs, shower areas, sinks, *etc.*) [8]. In such places, microbes can easily be transmitted to shampoo products, which are generally based on sodium lauryl sulphate surfactants that separate or discolor upon proliferation of *Pseudomonas* species [9]. Of special concern is detection of the latter pathogen that has spoilage potentials and is the most common microorganism associated with recall of many cosmetic formulations in the United States and Europe [4, 10,11].

Hence, antimicrobial ingredients are employed as antiseptics and (in lower concentrations) as preservatives for detergents [12]. Although the efficacy of a detergent is influenced by the formulation, the type and concentration of active ingredients are of particular importance[13,14]. A large number of chemical compounds have the ability to kill or inhibit the growth and metabolism of microorganisms [1]. Despite their rather large number, each antimicrobial has its own physical, chemical or toxicological limitations. So, the interest in development of new and better ones remains high [15]. One of the most efficient preservatives with powerful biocide effects is methylchloroisothiazolinone which is used in conjunction with methylisothiazolinone (MCI/MI) (Kathone CG) [16]. It is used in the manufacture

of cosmetics, detergents, paint, glue, and synthetic rubber and for disinfecting cooling systems. Kathone CG is known to be a potent sensitizer that may lead to the development of allergic contact dermatitis among cosmetics users and personnel working in industries where the substance is commonly used [17].

The emergence of nano-science and nanotechnology in the last decade has provided opportunities for exploring the bactericidal effects of metal nanoparticles [15,18]. Such effects have been attributed to their small size, and high surface to volume ratio, allowing them to interact closely with microbial membranes, coupled with the release of metal ions in solutions [19]. The antifungal and bacteriostatic properties of Ag NPs as well as the antimicrobial activity of Cu NPs, and Fe NPs have been reported [19-26]. Unlike antibiotics, NPs adaptation does not occur for microorganisms. These properties of Ag, Cu, Au, Fe, Zn, etc. nanoparticles can make them applicable in various fields; i.e., medical instruments and devices, water treatment and food processing [18-22,27].

This study investigates bactericidal efficacy of Ag, Cu, and Fe NPs against *Escherichia coli* (Gram negative), and *Staphylococcus aureus* (Gram positive) bacteria and potential application of the NPs as preservative in detergents including shampoo, hand washing liquid (HWL) and dish washing liquid (DWL).

MATERIALS AND METHODS
Preparation of Metal Nanoparticles
Metal NPs are prepared by DC-arc discharge method optimized in our group [28-30].

Silver electrodes, with an 80° angle, are exposed to pulses of 5-10 A/cm² in 10% glycerin/distilled water.

Pulses of 50 A/cm² are passed through Cu as well as Fe rods, with a 45° angle, in distilled water.

The resulting NPs are separated upon centrifuging and drying at 70 °C for 24 h. The XRD (Philips X'pert MPD, C_oK_α irradiation, λ = 1.78897 Å) at a scanning speed of 2°/min from, 20° to 80° (2θ)) SEM (KYKY EM3200- 25 KV), and TEM (ZEISS, EM10C, 80 KV), are used for depictions of crystalline structures, morphology and size of the metal NPs.

Preparation of Detergents/Metal NPs
The shampoo samples were prepared using distilled water, sodium luryl ether sulfate (SLES) as

surfactant, betain, glycerin, and coconut fatty acid. After mixing, pH was adjusted to neutral (6.5-7).

The HWL samples were formulated using four ingredients such as sodium luryl ether sulfate (SLES), betain, glycerin, coconut fatty acid and distilled water as vehicle. The pH of mixed solution was adjusted by adding sufficient quantity of citric acid solution (*p*H=6).

To formulate a basic DWL, definite amount of sulfonic acid and coconut fatty acid were added to distilled water. After mixing of the formulated DWL, the *p*H (6.5-7) was adjusted by adding diethanolamine.

Three samples of Ag NPs/detergent (0.1, 1.0, 10.0 g/L) were prepared by addition of 5, 50 and 500 mg of Ag NPs to three vials, containing 50 mL of detergent. Similarly, samples of Cu NPs as well as Fe NPs were prepared. Accordingly, twenty-seven different metal NPs/detergent vials were obtained (nine for any detergents). Each sample vial was placed in ultrasonic bath for 10 min until NPs are thoroughly dispersed. In order to compare the results, a commercial concentration of Kathone CG /detergent (50 mL) was also prepared (three vials).

Antibacterial Assay of Detergents/Metal NPs
Preservative capacity of the detergent samples was probed against detergent samples containing only Kathone CG. All of these thirty samples were contaminated with *E. coli* (ATCC 25922), and *S. aureus* (ATCC 25923) separately. Specifically, each of the above mentioned bacterial strains was cultured overnight on Muller-Hilton agar (ATCC, WDCM1). A suspension of each was prepared in 5 mL normal saline containing 10^9 cells/mL. These suspensions (100 μL) were mixed and homogenized with 500 μL detergent samples (60 samples). After a specific time, 5 mL sterile normal saline was added to these mixtures and vortexed for one minute. Dilutions of each tube were cultured on Muller-Hilton agar. The plates were maintained at 37 °C for 18 h. Finally, the number of colonies per sample was counted.

RESULTS AND DISCUSSION
Size, morphology, and durability of metal NPs highly depend on the method of synthesis. Following our quest for stable nanomaterials [28-32] and our recent interest in reaching for molded detergents with preservative and antibacterial applications, here we take up fabrication of durable metal nanoparticles, including Ag, Cu, and Fe

Table 1. Percentage growth (X) of E. coli and S. aureus in prepared detergent samples with Kathon CG and different concentrations of metal nanoparticles (NPs) after 1 h vicinage time.

			Shampoo				HWL				DWL	
	No.	[C]	X		No.	[C]	X		No.	[C]	X	
		(g/L)	*E. coli*	*S. aureus*		(g/L)	*E. coli*	*S. aureus*		(g/L)	*E. coli*	*S. aureus*
Ag NPs	1	0.1	543.48	12.78	4	0.1	0	12.73	7	0.1	54.35	0.00
	2	1	1304.35	0.00	5	1	0	5.91	8	1	195.65	0.00
	3	10	869.57	0.00	6	10	156.52	227.27	9	10	1.09	0.00
Cu NPs	10	0.1	0.00	0.00	13	0.1	521.74	0.00	16	0.1	695.65	0.00
	11	1	0.00	0.00	14	1	0.00	0.00	17	1	521.74	0.00
	12	10	0.00	0.00	15	10	0.00	0.00	18	10	0	0.00
Fe NPs	19	0.1	869.57	198.86	22	0.1	434.78	68.18	25	0.1	347.83	0.00
	20	1	521.74	109.09	23	1	695.65	43.18	26	1	521.74	0.00
	21	10	1043.48	68.18	24	10	760.87	34.09	27	10	108.70	0.00
Kathon CG	28	1	10.87	1.48	29	1	8.70	11.36	30	1	5.65	0.00

NPs, through arc discharge. They are mixed (in 3 concentrations) with shampoo, HWL and DWL formulations.

Fabrication of Durable Metal NPs Through Arc Discharge

Our DC arc discharge technique involves explosion of metal rods by a pulse current. Fairly pure metal electrodes (99%) with diameters of 2 mm and lengths of 40 mm were used as anode and cathode. Explosion of silver, copper and iron rods occur at a pulse current of 5-10, 50 and 50 A/cm^2, respectively. Average particle size for Ag, Cu and Fe NPs appears as small as 8, 20 and 37nm based on their TEM images respectively (see supplementary file).

Antibacterial Assay of Shampoo, HWL and DWL Formulations/Metal Nanoparticles

Preservative capacities of Ag, Cu, Fe NPs are probed for twenty-seven samples with three different concentrations of metal nanoparticles and compared to those of three samples containing only Kathone CG. All the above samples were separately tested against deliberate contamination with *E. coli*, and *S. aureus*. Specifically, each of the above mentioned bacterial strains was cultured overnight on Muller-Hilton agar. A suspension of each was prepared in 5 mL normal saline containing 10^9 cells/mL. Then, 100 μL of each suspension of bacteria was separately added to 500 μL of each of the thirty detergent samples. Consequently, the above samples were homogenized *via* a shaker. After 24 hours, 5 mL sterile normal saline was added to these mixtures and vortexed for one minute. Three dilutions of each sample (1, 0.1, and 0.01 *v/v*) were cultured on Muller-Hilton agar. The 90 plates were maintained at 37°C for 18 h, and then the number of colonies per sample was counted. The overnight vicinity (24 h) shampoo, HWL and DWL samples extirpated all of the bacteria. Hence, vicinage time was gradually decreased and experiments were repeated down to 12 and then 6 h, where all the bacteria were similarly extirpated. So, the time was decreased again. After 1 h and in dilution of 0.01 *v/v*, alterations were observable and results were recorded (Table 1).

Quantitatively, these results are based on the percent bacterial growth (X), shown by X= $(1-((B-T)/B)) \times 100$. Here, B is the number of colonies in a bacterial assay used as the "Control" (Sample B). "Control" is attributed to every one of the two strains of bacteria directly cultured on agar, without being subjected to the shampoo, HWL and DWL formulations. T is the number of colonies found in either one of the thirty detergent samples.

9 detergent samples containing three concentrations of Ag NPs (0.1, 1.0 and 10.0 g/L) were investigated. The bactericidal efficiency of these products (samples 1-9) was studied against *E. coli* and *S. aureus*. Based on the results, Ag NPs with either of its three concentrations in shampoo and DWL samples show an efficient antibacterial activity against *S. aureus* (Fig. 1a and 1c), while in HWL in concentration of 10 g/L it does not show a good efficiency (Fig. 1b).

The results for *E. coli* are completely different especially in shampoo samples. X values are really large in all shampoo samples (Fig. 1a). The results of assessment of antibacterial potency (Fig. 1b) revealed that Ag NPs (0.1, 1.0 g/L) in HWL and (0.1, 10 g/L) in DWL have potent antibacterial activities
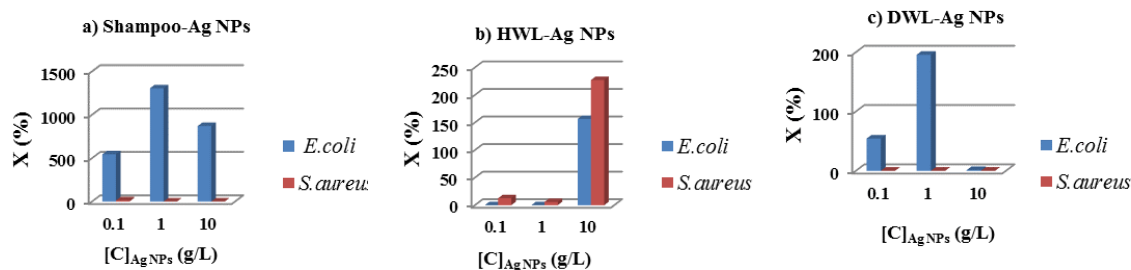
Fig.1. Percentage growth of bacteria vs. concentration of Ag NPs a) shampoo b) HWL and c) DWL samples.

against *E. coli* cells. This efficacy at concentration of 10.0 g/L HWL and 1.0 g/L DWL decreased. Here, *S. aureus* is more sensitive than *E. coli* to the Ag NPs, suggesting that *E. coli* is more resistant to Ag NPs. Outer membrane of Gram- negative bacteria is mostly formed from lipopolysaccharide molecules causing a resistance barrier against nanoparticles [33]. It is known that possible free silver ion (Ag^+), and those Ag^+ and Ag^0 can be released by Ag NPs (eq. 1) which are highly toxic to bacteria [34-36]. On the other hand, bacterial cell wall has a negative charge because of teichoic acids (in Gram positive bacteria) linked to either the peptidoglycan or to the underlying plasma membrane and outer covering of phospholipids and Lipopolysaccharides (in Gram negative) [37]. This negative charge (9.57 r/e (-)) in *S. aureus* is really more than that in *E. coli* (1.33 r/e (-)) [38]. So, released Ag^+ ion can easily connect to *S. aureus* cells wall and may affect them through deactivation of cellular enzymes and DNA by reacting with electron-donating groups such as thiol (–SH) groups and generates ROS ultimately leading to cell lysis and death [39-44]. Although, the antimicrobial mechanistic action of Ag NPs is not clearly understood, previous research has demonstrated that Ag NPs attach the surface of cell membrane, causing the change of membrane permeability, dissipation of the ATP pool and proton motive force, bringing about the final cell death [44-47]. Some studies suggest that *E. coli* cells may have stronger oxidizing/reducing power and interact with Ag species to form cell-particle aggregates [39,45,48]. To study the effect of Ag^+ on *E. coli* and *S. aureus*, Ag^+ (released from Ag NPs during 6 months) in three concentrations in studied detergents was used (Table 2).

The results of antibacterial assay in shampoo and DWL samples show that with increasing Ag^+ concentration, growth of *E. coli* increases, but in the HWL samples *E. coli* growth falls due to raising the Ag^+ concentration (Fig. 2).

The results show Ag^+ ions, even at very low concentration, eliminate all *S. aureus* cells and show that this bacterium is really sensitive to Ag+ ions even in a very low concentration.

$$4Ag + O_2 + 2H_2O \rightarrow 4Ag^+ + 4HO^-$$
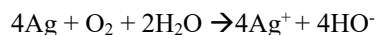
In Cu NPs study, 9 formulated detergents involving three different concentrations of Cu NPs (0.1, 1.0 and 10.0 g/L shampoo, HWL and DWL formulations) were investigated. The bactericidal effects of these products (Table 1, samples10-18) were studied against *E. coli* and *S. aureus*. Fortunately, all bacteria were extirpated in all shampoo samples (Fig. 3a). Based on the results of antibacterial efficacy tests of HWL (Fig. 3b), it can be perceived that presence of Cu NPs (1.0, and 10.0 g/L HWL formulation) completely inhibited growth of both *E. coli* and *S. aureus*. The antibacterial tests of DWL conducted using Cu NPs proved that the Cu NPs have high antibacterial efficiency against *S. aureus*. However, maximum efficiency of 100 % against *E. coli* strain was observed in sample 18 with 10.0g/L Cu NPs in DWL formulation (Fig. 3c).

Hence, Cu NPs could be considered as a potential antibacterial agent against *E. coli* strain. The elimination percentage of this bacterium increased with raising quantity of Cu NPs. Among various metal nanoparticles, Cu NPs is said to have attracted more attention because of its antifungal/antibacterial properties [19,23,24,49-51]. The bactericidal effect of Cu NPs is attributed to their small size, and high surface to volume ratio, enabling them to interact closely with microbial membranes [19,46]. Bacteria exhibit differential sensitivities to different Cu species. Gram positive bacteria are more sensitive than Gram negative bacteria [52]. The exact mechanism of antimicrobial action of Cu NPs is not clearly reported and the general view seems to be a combination of several factors

Table 2. Percentage growth (X) of E. coli and S. aureus after 1 h vicinage time in prepared detergent samples with Ag⁺ ions released from Ag NPs in distilled water during 6 months.

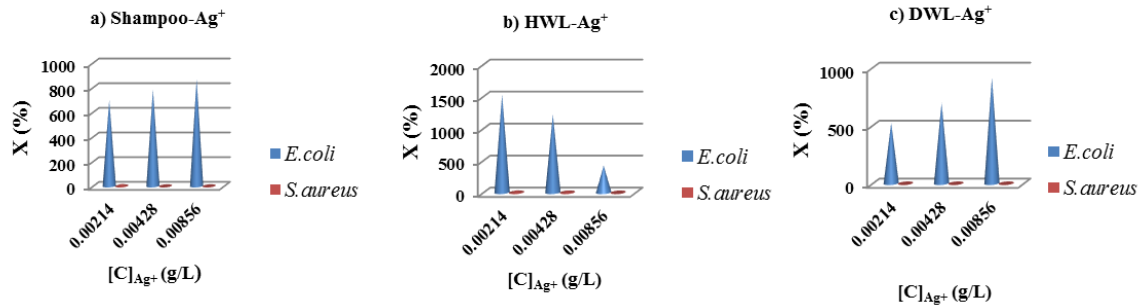|			Shampoo				HWL				DWL	
	No.	[C] (g/L)	X		No.	[C] (g/L)	X		No.	[C] (g/L)	X	
			E. coli	S. aureus			E. coli	S. aureus			E. coli	S. aureus
Ag⁺ ions	31	0.00214	695.65	15.91	34	0.00214	1521.74	31.25	37	0.00214	521.74	0
	32	0.00428	782.61	0.45	35	0.00428	1217.39	28.41	38	0.00428	695.65	0
	33	0.00856	869.57	4.55	36	0.00856	417.39	0	39	0.00856	913.04	0

Fig. 2. Percentage growth of bacteria vs. concentration of silver ions released from silver nanoparticles (Ag NPs) a) shampoo, b) HWL, and c)DWL samples
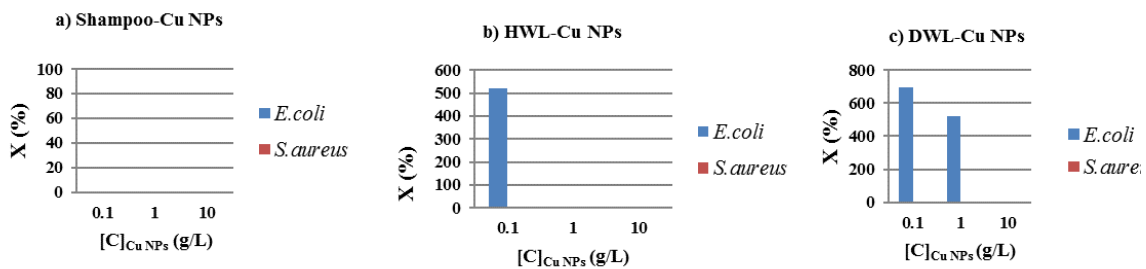

Fig. 3. Percentage growth of bacteria vs. concentration of copper nanoparticles (Cu NPs) a) shampoo, b) HWL, and c) DWL samples.

including: released Cu^{2+} ions in the solution from Cu NPs and consequent changes in pH and conductivity, direct penetration and disruption of cell membrane by Cu^{2+} ions, DNA damage and disruption of biochemical pathway by chelating cellular enzymes, *etc*. The above have been reported to occur simultaneously during interactions with microbial cells, where Cu^{2+} exerts antimicrobial effect on the freely moving bacteria [18,24,53-56].

To study Fe NPs in detergents, 9 formulated detergents including shampoo, HWL and DWL formulations with three different concentrations of Fe NPs (0.1, 1.0 and 10.0 g/L) were investigated. The bactericidal effects of these products (Table 1, samples 19-27) were studied against *E. coli* and *S. aureus*(Fig.4). The antibacterial activity of Fe NPs in shampoo samples is frustrating at 1 h vicinage time especially against *E. coli* (Fig. 4a). Even in

HWL, the results for *E. coli* are not reasonable, while the X values of *S. aureus* are acceptable (Fig. 4b). In DWL samples, *E. coli* cells growth is high but not as much as shampoo and HWL samples (Fig. 4c).

The best results for Fe NPs antibacterial activity is against *S. aureus* in DWL samples which all cells were extirpated in all concentrations studied. As to the mechanism involved, the released ions by Fe NPs may attach to the negatively charged bacterial cell wall and rupture it, thereby leading to protein denaturation and cell death [57,58]. Also, Fe^{2+} may react with intracellular oxygen or hydrogen peroxide and produce reactive oxygen species which may have induced oxidative stress and inflammatory responses [59-61]. Moreover, such cellular processes may lead to cell death *via* cell necrosis or apoptosis [58]. In a short time, releasing Fe^{2+} or Fe^{3+} ions from Fe NPs is more difficult
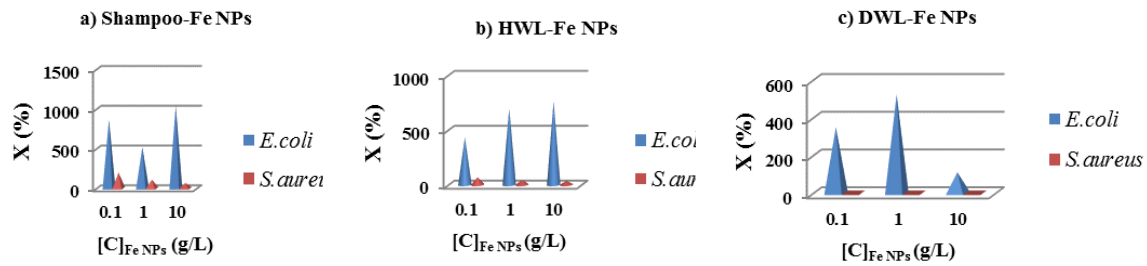
174

Fig. 4 Percentage growth of bacteria vs. concentration of iron nanoparticles (Fe NPs) a) shampoo, b) HWL, and c) DWL samples.
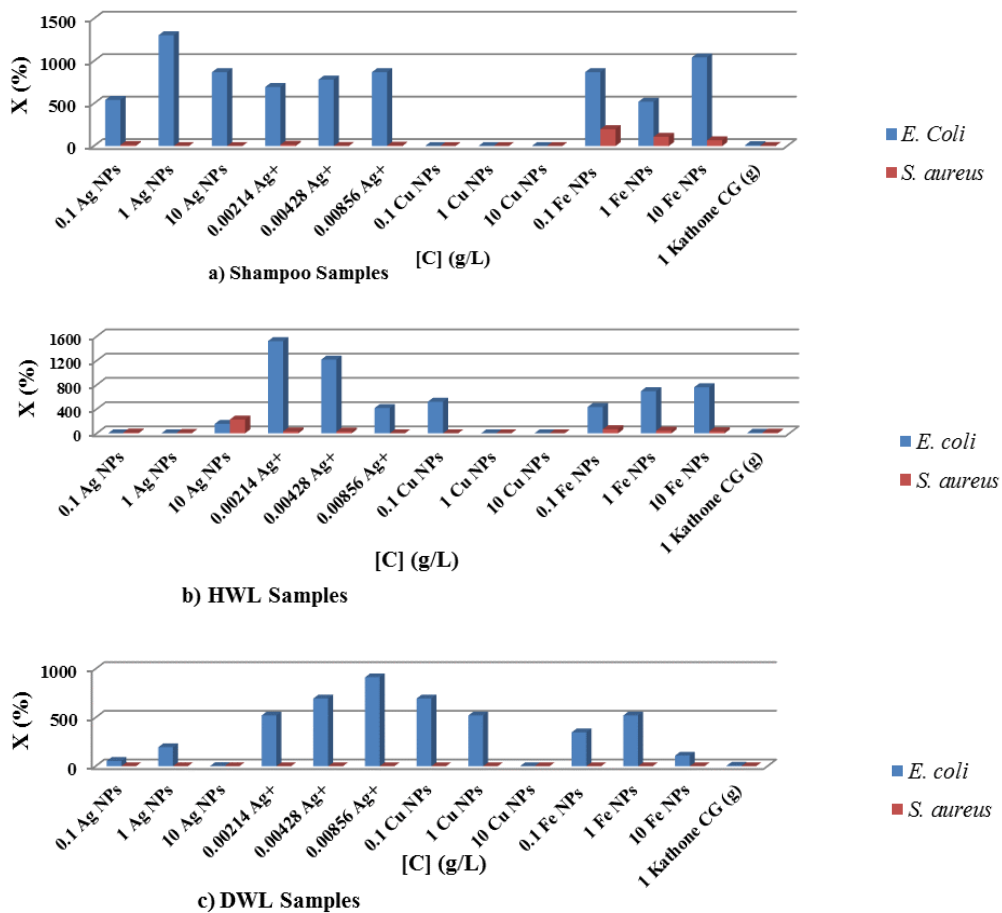

Fig. 5 Percentage growth of bacteria vs. concentration of different preservatives a) shampoo, b) HWL, and c) DWL samples.

because of the redox potential, so, antibacterial activity of Fe NPs is less than Ag and Cu NPs in this study.

Although all of the studied metallic NPs exhibit excellent antibacterial efficiency in the time of more than 1 h, in short vicinage time, growth of cells especially in *E. coli* increased and there is not any special order for that. Since the detergents contain one or more surfactants, they help growth

of bacteria in short time after contamination [62,63]. Comparing the antibacterial assay of NPs in time tested (Fig. 5) shows Cu NPs have an average best activity against *E. coli* and *S. aureus* in shampoo, HWL, and DWL samples and the order of antibacterial activity of these preservatives is:

Cu NPs>Ag NPs> Fe NPs.

Based on using minimum amount of NPs,

shampoo samples with 0.1 g/L Cu NPs and HWL and DWL with 0.1 g/L Ag NPs indicate outstanding results against considered *E. coli* and *S. aureus* strains. Among different detergents, *S. aureus* cells approximately were extirpated in all DWL samples that may be due to chemical make-up of DWL formulation.

CONCLUSION

This study clearly demonstrates the advantages of using rather low concentrations of Ag, Cu and Fe NPs as preservatives

instead of carcinogenic Kathone CG, which is commonly used in detergent products. The shampoo formulation with 0.1 g/L

Cu NPs and HWL and DWL with 0.1 g/L Ag NPs exhibit the best antibacterial activity against tested *E. coli* and *S. aureus.* Conclusively, the order of antibacterial activity on these preservatives was: Cu NPs>Ag NPs> Fe NPs.

ETHICAL APPROVAL

This study was funded by the Iran National Science Foundation (INSF).

This article does not contain any studies with human participants or animals performed by any of the authors.

REFERENCES

1. Bhat R, Prajna P, Menezez VP, Shetty P. Antimicrobial activities of soap and detergents. Adv Biores. 2011;2(2):52-62.
2. Abu Shaqra Q MY, Al-Momani W. . Microbiological quality and in use preservative capacity of shampoo preparations manufactured in Jordan. Jordan Journal of Biological Sciences. 2011;4(2):113-8.
3. Nadagouda MN, Speth TF, Varma RS. Microwave-Assisted Green Synthesis of Silver Nanostructures. Accounts of Chemical Research. 2011;44(7):469-78.
4. Mallick K, Witcomb M, Scurrell M. Silver nanoparticle catalysed redox reaction: An electron relay effect. Materials Chemistry and Physics. 2006;97(2-3):283-7.
5. Carlotti D-N, Gatto H. Die Anwendung von Shampoos zur Therapie und Prophylaxe dermatologischer Erkrankungen bei Hund und Katze. Kleintierpraxis. 2004;49(7):447-58.
6. Kloos I, Straubinger RK, Werckenthin C, Mueller RS. Residual antibacterial activity of dog hairs after therapy with antimicrobial shampoos. Veterinary Dermatology. 2013;24(2):250-e54.
7. Philip D. Rapid green synthesis of spherical gold nanoparticles using Mangifera indica leaf. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 2010;77(4):807-10.
8. Tien D, Liao C, Huang J, Tseng K, Lung J, Tsung T, et al. Novel technique for preparing a nano-silver water suspension by the arc-discharge method. Rev Adv Mater Sci. 2008;18:750-6.
9. Murugan E, Jebaranjitham JN. Synthesis and characterization of silver nanoparticles supported on surface-modified poly(N-vinylimidazale) as catalysts for the reduction of 4-nitrophenol. Journal of Molecular Catalysis A: Chemical. 2012;365:128-35.
10. Zheng J, Nicovich PR, Dickson RM. Highly Fluorescent Noble-Metal Quantum Dots. Annual Review of Physical Chemistry. 2007;58(1):409-31.
11. Kelly KL, Coronado E, Zhao LL, Schatz GC. The Optical Properties of Metal Nanoparticles: The Influence of Size, Shape, and Dielectric Environment. ChemInform. 2003;34(16).
12. Marzulli F, Maibach H. Antimicrobials: experimental contact sensitization in man. J Soc Cosmet Chem. 1973;24:399-421.
13. Lloyd H, Lamport AI. Activity of chlorhexidine shampoos in vitro against Staphylococcus intermedius, Pseudomonas aeruginosa and Malassezia pachydermatis. Veterinary Record. 1999;144(19):536-7.
14. Young R, Buckley L, McEwan N, Nuttall T. Comparative in vitro efficacy of antimicrobial shampoos: a pilot study. Veterinary Dermatology. 2011;23(1):36-e8.
15. Pant G, Nayak N, Gyana Prasuna R. Enhancement of antidandruff activity of shampoo by biosynthesized silver nanoparticles from Solanum trilobatum plant leaf. Applied Nanoscience. 2012;3(5):431-9.
16. Hunziker N. The 'Isothiazolinone Story'. Dermatology. 1992;184(2):85-6.
17. Monsálvez V, Fuertes L, Ortiz de Frutos J, Vanaclocha F. Sensitization to Methylchloroisothiazolinone-Methylisothiazolinone After a Burn Caused by Massive Accidental Occupational Exposure. Actas Dermo-Sifiliográficas (English Edition). 2011;102(3):224-6.
18. Ruparelia JP, Chatterjee AK, Duttagupta SP, Mukherji S. Strain specificity in antimicrobial activity of silver and copper nanoparticles. Acta Biomaterialia. 2008;4(3):707-16.
19. Ramyadevi J, Jeyasubramanian K, Marikani A, Rajakumar G, Rahuman AA. Synthesis and antimicrobial activity of copper nanoparticles. Materials Letters. 2012;71:114-6.
20. Lee C, Sedlak DL. Enhanced Formation of Oxidants from Bimetallic Nickel−Iron Nanoparticles in the Presence of Oxygen. Environmental Science & Technology. 2008;42(22):8528-33.
21. Auffan Ml, Achouak W, Rose Jr, Roncato M-A, Chanéac C, Waite DT, et al. Relation between the Redox State of Iron-Based Nanoparticles and Their Cytotoxicity towardEscherichia coli. Environmental Science & Technology. 2008;42(17):6730-5.
22. Mahdy SA, Raheed QJ, Kalaichelvan P. Antimicrobial activity of zero-valent iron nanoparticles. International Journal of Modern Engineering Research. 2012;2(1):578-81.
23. Yoon K-Y, Hoon Byeon J, Park J-H, Hwang J. Susceptibility

constants of Escherichia coli and Bacillus subtilis to silver and copper nanoparticles. Science of The Total Environment. 2007;373(2-3):572-5.

24. Cioffi N, Torsi L, Ditaranto N, Tantillo G, Ghibelli L, Sabbatini L, et al. Copper Nanoparticle/Polymer Composites with Antifungal and Bacteriostatic Properties. Chemistry of Materials. 2005;17(21):5255-62.

25. Panáček A, Kvítek L, Prucek R, Kolář M, Večeřová R, Pizúrová N, et al. Silver Colloid Nanoparticles: Synthesis, Characterization, and Their Antibacterial Activity. The Journal of Physical Chemistry B. 2006;110(33):16248-53.

26. Guzmán MG, Dille J, Godet S. Synthesis of silver nanoparticles by chemical reduction method and their antibacterial activity. Int J Chem Biomol Eng. 2009;2(3):104-11.

27. Joo SH, Feitz AJ, Sedlak DL, Waite TD. Quantification of the Oxidizing Capacity of Nanoparticulate Zero-Valent Iron. Environmental Science & Technology. 2005;39(5):1263-8.

28. Miranzadeh M, Kassaee MZ. Solvent effects on arc discharge fabrication of durable silver nanopowder and its application as a recyclable catalyst for elimination of toxic p-nitrophenol. Chemical Engineering Journal. 2014;257:105-11.

29. Kassaee MZ, Buazar F, Motamedi E. Effects of Current on Arc Fabrication of Cu Nanoparticles. Journal of Nanomaterials. 2010;2010:1-5.

30. Kassaee MZ, Motamedi E, Mikhak A, Rahnemaie R. Nitrate removal from water using iron nanoparticles produced by arc discharge vs. reduction. Chemical Engineering Journal. 2011;166(2):490-5.

31. Kassaee MZ, Motamedi E, Majdi M, Cheshmehkani A, Soleimani-Amiri S, Buazar F. Media effects on nanobrass arc fabrications. Journal of Alloys and Compounds. 2008;453(1-2):229-32.

32. Kassaee MZ, Buazar F. Al nanoparticles: Impact of media and current on the arc fabrication. Journal of Manufacturing Processes. 2009;11(1):31-7.

33. Brayner R, Ferrari-Iliou R, Brivois N, Djediat S, Benedetti MF, Fiévet F. Toxicological Impact Studies Based onEscherichiacoliBacteria in Ultrafine ZnO Nanoparticles Colloidal Medium. Nano Letters. 2006;6(4):866-70.

34. Kawashita M, Tsuneyama S, Miyaji F, Kokubo T, Kozuka H, Yamamoto K. Antibacterial silver-containing silica glass prepared by sol–gel method. Biomaterials. 2000;21(4):393-8.

35. Radheshkumar C, Münstedt H. Antimicrobial polymers from polypropylene/silver composites—Ag+ release measured by anode stripping voltammetry. Reactive and Functional Polymers. 2006;66(7):780-8.

36. Miranzadeh M, Kassaee MZ, Sadeghi L, Sadroddini M, Razzaghi Kashani M, Khoramabadi N. Antibacterial ethylene propylene rubber impregnated with silver nanopowder: AgNP@EPR. Nanochemistry Research. 2016;1(1):1-8.

37. Koprivnjak T, Peschel A, Gelb MH, Liang NS, Weiss JP. Role of Charge Properties of Bacterial Envelope in Bactericidal Action of Human Group IIA Phospholipase A2againstStaphylococcus aureus. Journal of Biological Chemistry. 2002;277(49):47636-44.

38. Dickson JS, Koohmaraie M. Cell surface charge characteristics and their relationship to bacterial attachment to meat surfaces. Applied and Environmental Microbiology. 1989;55(4):832-6.

39. Choi O, Deng KK, Kim N-J, Ross L, Surampalli RY, Hu Z. The inhibitory effects of silver nanoparticles, silver ions, and silver chloride colloids on microbial growth. Water Research. 2008;42(12):3066-74.

40. Gogoi SK, Gopinath P, Paul A, Ramesh A, Ghosh SS, Chattopadhyay A. Green Fluorescent Protein-ExpressingEscherichiacolias a Model System for Investigating the Antimicrobial Activities of Silver Nanoparticles. Langmuir. 2006;22(22):9322-8.

41. Matsumura Y, Yoshikata K, Kunisaki Si, Tsuchido T. Mode of Bactericidal Action of Silver Zeolite and Its Comparison with That of Silver Nitrate. Applied and Environmental Microbiology. 2003;69(7):4278-81.

42. Sambhy V, MacBride MM, Peterson BR, Sen A. Silver Bromide Nanoparticle/Polymer Composites: Dual Action Tunable Antimicrobial Materials. Journal of the American Chemical Society. 2006;128(30):9798-808.

43. Ratte HT. Bioaccumulation and toxicity of silver compounds: A review. Environmental Toxicology and Chemistry. 1999;18(1):89-108.

44. Choi O, Hu Z. Size Dependent and Reactive Oxygen Species Related Nanosilver Toxicity to Nitrifying Bacteria. Environmental Science & Technology. 2008;42(12):4583-8.

45. Sondi I, Salopek-Sondi B. Silver nanoparticles as antimicrobial agent: a case study on E. coli as a model for Gram-negative bacteria. Journal of Colloid and Interface Science. 2004;275(1):177-82.

46. Morones JR, Elechiguerra JL, Camacho A, Holt K, Kouri JB, Ramírez JT, et al. The bactericidal effect of silver nanoparticles. Nanotechnology. 2005;16(10):2346-53.

47. Lok C-N, Ho C-M, Chen R, He Q-Y, Yu W-Y, Sun H, et al. Proteomic Analysis of the Mode of Antibacterial Action of Silver Nanoparticles. Journal of Proteome Research. 2006;5(4):916-24.

48. Kahraman M, Yazici MM, Slahin F, Bayrak ÖF, Çulha M. Reproducible Surface-Enhanced Raman Scattering Spectra of Bacteria on Aggregated Silver Nanoparticles. Applied Spectroscopy. 2007;61(5):479-85.

49. Ponce AA, Klabunde KJ. Chemical and catalytic activity of copper nanoparticles prepared via metal vapor synthesis. Journal of Molecular Catalysis A: Chemical. 2005;225(1):1-6.

50. Huang Z, Cui F, Kang H, Chen J, Zhang X, Xia C. Highly Dispersed Silica-Supported Copper Nanoparticles Prepared by Precipitation−Gel Method: A Simple but Efficient and Stable Catalyst for Glycerol Hydrogenolysis. Chemistry of Materials. 2008;20(15):5090-9.

51. Wei Y, Chen S, Kowalczyk B, Huda S, Gray TP, Grzybowski BA. Synthesis of Stable, Low-Dispersity Copper Nanoparticles and Nanorods and Their Antifungal and Catalytic Properties. The Journal of Physical Chemistry C. 2010;114(37):15612-6.

52. Kaweeteerawat C, Chang CH, Roy KR, Liu R, Li R, Toso D, et al. Cu Nanoparticles Have Different Impacts in Escherichia coli and Lactobacillus brevis than Their Microsized and Ionic Analogues. ACS Nano. 2015;9(7):7215-25.

53. Onodera Y, Sunayama S, Chatterjee A, Iwasaki T, Satoh T, Suzuki T, et al. Bactericidal allophanic materials prepared from allophane soil. Applied Clay Science. 2001;18(3-4):135-44.

54. Ren G, Hu D, Cheng EWC, Vargas-Reus MA, Reip P, Allaker RP. Characterisation of copper oxide nanoparticles

for antimicrobial applications. International Journal of Antimicrobial Agents. 2009;33(6):587-90.

55. Noyce JO, Michels H, Keevil CW. Potential use of copper surfaces to reduce survival of epidemic meticillin-resistant Staphylococcus aureus in the healthcare environment. Journal of Hospital Infection. 2006;63(3):289-97.

56. Bagchi B, Dey S, Bhandary S, Das S, Bhattacharya A, Basu R, et al. Antimicrobial efficacy and biocompatibility study of copper nanoparticle adsorbed mullite aggregates. Materials Science and Engineering: C. 2012;32(7):1897-905.

57. Lin Y-sE, Vidic RD, Stout JE, McCartney CA, Yu VL. Inactivation of Mycobacterium avium by copper and silver ions. Water Research. 1998;32(7):1997-2000.

58. Selvarani M, Prema P. Evaluation of antibacterial efficacy of chemically synthesized copper and zerovalent iron nanoparticles. Asian J Pharm Clin Res. 2013;6(3):222-7.

59. Huang G, Chen H, Dong Y, Luo X, Yu H, Moore Z, et al. Superparamagnetic Iron Oxide Nanoparticles: Amplifying ROS Stress to Improve Anticancer Drug Efficacy. Theranostics. 2013;3(2):116-26.

60. Lee C, Kim JY, Lee WI, Nelson KL, Yoon J, Sedlak DL. Bactericidal Effect of Zero-Valent Iron Nanoparticles on Escherichia coli. Environmental Science & Technology. 2008;42(13):4927-33.

61. Wei D, Sun W, Qian W, Ye Y, Ma X. The synthesis of chitosan-based silver nanoparticles and their antibacterial activity. Carbohydrate Research. 2009;344(17):2375-82.

62. Miranzadeh M, Kassaee MZ, Sadeghi L. Analysis of Preservative Capacity for Contemporary Iranian Shampoos. Advanced Journal of Chemistry, Section A: Theoretical, Engineering and Applied Chemistry. 2019;2(Issue 1):45-56.

63. Kusumaningrum HD, van Putten MM, Rombouts FM, Beumer RR. Effects of Antibacterial Dishwashing Liquid on Foodborne Pathogens and Competitive Microorganisms in Kitchen Sponges. Journal of Food Protection. 2002;65(1):61-5.