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RESEARCH ARTICLE OPEN ACCESS

Silver doped micro porous Zeolitic materials for antimicrobial applications

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ABSTRACT
In association with upcoming energy demand and fossil fuel crises fastidiously in India; Co–firing i.e. combustion of coal and biomass (rice husk) is gaining considerable attention. The leftover during the process is termed as composite ash consisting amorphous silica as major component. As reputable, Zeolites or Molecular sieves are crystalline hydrated alumino-silicate resin historically known for its unique permeable bare bones which is also an overruling material as ion exchanger, adsorbent and catalyst in chemical reaction. Synthesis of MS-4A from composite ash, silver doping, its physicochemical and analytical characterizations as well as antimicrobial activity are reported in this paper.
For silver doping aimed at MS 4A, ion exchange was found to be predominant method reported in literature. Antimicrobial activity of silver doped sample was experimentally justified against gram-negative bacteria. The current paper also deals with the way to methodize formation of MS 4A by amalgamating waste aluminium scrap extricate tuned with sodium silicate extracted using ash followed by hydrothermal crystallization. Fair amount of hydrogen gas liberated in the process can be a gainful utility in other chemical industries.
Keywords: Composite ash, MS 4A, Silver, Antimicrobial, Waste

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I. INTRODUCTION

Due to constantly mounting population of our country, there is amplified call for energy. Excessive amount of coal is burned for satisfying necessity of the energy. The amount of an ash generated by coal-based thermal power plants has been swelling at a disturbing rate throughout the world **[1]**. The current grade of coal used in combustion is producing nearly 40-45% ash ensuing generation of 169.25 million tons averagely in year 2018**[2]**. It has been also observed that the fly ash generates as a result of coal firing is polluting three major sectors of environment (air, water and land) predominantly hence reflected as ironic source of pollution. To resolve this issue, it has been proposed to produce energy economically using biomass resources **[3-4]**. Numerous forms of biomass such as wheat, sugarcane, corn, eucalyptus etc. are currently obtainable in our country. India being second largest manufacturer of rice paddies globally, the ample and ease in availability of rice husk makes it an appropriate biomass for co-firing **[5]**. Also, the calorific value of rice husk is nearly two third that of coal and hence mini thermal power plants have already been started in various states of India such as Chhattisgarh and Utter Pradesh producing nearly 8 to 15 MW energy **[6]**. The ash generated from these power plants is termed as Composite Ash (CA) as it is an outcome of co-firing of coal and biomass. On stuffing the composition of this ash, it was found that it contained silica about 85-90% in amorphous form which is easier to disintegrate. Hence composite ash was identified as a major source of silica as well as of sodium silicate which is the key material for Zeolites or Molecular Sieves.

Zeolites or MS 4A with tangled micro porosity have been studied as a prominent class of industrial porous materials **[7]**. MS 4A are noted for their liability toward their ion exchange and reversible dehydration. They have framework

structure that encloses interconnected cavities occupied by large number of metal cations (frequently Na) and water molecules **[8]**. MS 4A is a typical 3D hydrated aluminosilicate gel basically structured as 0. $2Na_2O.xSiO_2$: $yAl_2O_3.zH_2O$; where x/y ratio is ranging between 1.0 - 1.2 [**9]**. Non toxicity, high ion exchange capacity, functional molecular sieve & uniform porous structure are the prominent elite properties sustained by MS 4A because of which it has wide demand in detergent and accompanying industries **[10]**.

In addition to earlier work, our key objective is to prepare MS 4A with antibacterial characteristics via doping the silver particles on the structure of MS 4A. The transition metals are attractive because of their exclusive physicochemical properties **[11]**. Silver (Ag) also originates under transition element has several applications in various regions such as food industries, medicine, clothing, dentistry, catalysis, electronics, optics, mirrors and photography. As we all are aware, Ag with powerful antibacterial activity and a broad antibacterial spectrum has been widely used as antibacterial agents, and the antibacterial activities of silver ions and silver nanoparticles has been extensively researched**[12]**, when Ag entered the environment, probably because of the engagement with the DNA of bacteria, the reproduction of bacteria caused interfered, furthermore, the positively charged silver ions could interact with cell wall (mostly negatively charged) and led to the breakage of cell wall **[13]**. The largest advantage of silver antimicrobials is that silver can be easily incorporated in a carrier support material such as polymers, metal oxides, silica, clays, synthetic and natural MS 4A **[14-21]**. This is a more cost-effective alternative than the direct use of silver compounds such as silver nitrate solution and silver plate **[22, 23]**. Ag+ can be immobilized on MS 4A due to its micro-porous frameworks structure and excellent ions binding capacity **[24]**. For doping purpose, ion exchange method was approached. Besides the different pore size and shape, the hydrophilic/hydrophobic nature of MS 4As renders them as useful selective sorbents and hosts for guest molecules (organic or inorganic) that are stable in gas and liquid phase **[25]**. Silver-loaded MS 4A is so safe, heat-resistant, durable and good reason that a considerable amount of works has been devoted to this popular subject **[26]**. In the fully Ag+ exchanged MS 4A (Ag- MS 4A) the 12 Ag+ ions are present inside the MS 4A cages, as needed to balance the anionic charge of the MS 4A framework **[27]**.The existence of silver ions has been investigated by X-ray diffraction experiments with variable doping concentration. This silver doped MS 4A was found to be effective and effectual in wide-ranging abolition of E. coli. This was comprehensively examined by antimicrobial tests. These microorganisms were chosen because of the condition that they exist in numerous fields like water **[28, 29]**, food material **[30]** and medical environment which cause environmental threats.

Nevertheless, from last several decades numerous hydrothermal techniques were suggested and studied for the synthesis of MS 4As using flyash, kaolinite, diatomite and perlite as an inexpensive source. Usually the processes were carried out by varying some of the effective parameters including nucleating temperature and concentration of organic template, aging and crystallization time to dominate the nucleation phenomenon over crystal growth **[31]**. The current paper broadly highlights on enhancement of the repellence of the silver doped CA based MS 4A which also wires the necessity of improvement of the antimicrobial activity from the previous work. Not only the repellence but also the utilization of the solid waste i.e. aluminium scrap produced from industries for the manufacturing sodium aluminate being one of the major raw material required in the synthesis of MS 4A. The evolution of hydrogen supports the monetary purpose of the process is illuminated in further context.

II. MATERIALS AND METHODOLOGY

The alkali source and silver nitrate salt were procured from MERCK India and Himedia Laboratories. Aqueous Sodium Silicate containing 16% SiO_2 was procured from NCSR Chemicals Pvt. Ltd, near Nagpur district while aluminium scrap was collected from Automobile sector MIDC, Hingna. De-ionized water used in the synthesis was prepared using laboratory grade double distillation unit. Doping of Silver ions on MS-4A matrix was carried out with the help of laboratory shaker from Murhopye scientific company. The flocculation unit (Make: SECOR India) was utilised for agitation. Drying was performed with the help of laboratory oven from SENTWIN Company. Vacuum pump (Make: SUPERFIT) was utilized for vacuum filtration. Hydrothermal crystallization was carried out in a Teflon lined pressure vessel with a capacity of 300 ml. Microporous filter paper (41) from Himedia laboratories have been used to separate solid product from mother liquor.

III. EXPERIMENTAL

3.1 Synthesis of sodium aluminate and MS 4A

Initially aqueous Sodium aluminate was prepared using aluminium scrap by alkali extraction method. Here 8g dried mass of metal scrap was mixed with 1.5N NaOH solution in 1:20-22 ratio (W/W) and reflux for 1.5hour using ghram condenser. The residue was separated using microporous filter paper to acquire sodium aluminate solution. To this pre-calculated volume of sodium silicate was added in to get gel composition desired to formulate MS 4A. The resultant gel was later agitated using flocculation unit for 4-6h followed by hydrothermal crystallisation using Teflon lined SS autoclave for 3-4h at 100°C. After this the crystalline product was filtered and washed thoroughly with de ionised water and dried using laboratory oven at 60°C for overnight **[32]**. Similar attempts were carried out with variable composition of sodium aluminate and hydrothermal crystallisation time. The as such prepared samples were further analysed for their ion exchange capacity as per method reported in literature **[33]** and the results are reported in **Table 1.**

Table 1- Reaction Parameters for the synthesis of CA based MS 4A samples

Sample Id	Sodium silicate (g)	Sodium aluminate (g)	Aging (h)	Hydrothermal crystallization (h)	Temperature (°C)	CBC (Meq/100 g)
MS 4A -1	52.5	181	6	2-2.5	110-120	405
MS 4A -2	52.5	181	6	3-3.5	110-120	475
MS 4A -3	52.5	181	6	4-4.5	110-120	462
MS 4A -4	52.5	186	6	2-2.5	110-120	420
MS 4A -5	52.5	186	6	3-3.5	110-120	508
MS 4A -6	52.5	186	6	4-4.5	110-120	486
MS 4A -7	52.5	191	6	2-2.5	110-120	469
MS 4A -8	52.5	191	6	3-3.5	110-120	504
MS 4A -9	52.5	191	6	4-4.5	110-120	493
Commercial Standard	-	-	-	-	-	520

From the results, it has been established that the sample (MS 4A-5) was standing with highest ion exchange capacity; henceforth the same was subjected towards further instrumental investigations such as X-Ray Diffraction and FTIR to study the crystalline framework, **Figure 1** and **Figure 2** represent the infrared spectrogram and X-ray diffractogram of MS 4A-5 sample correspondingly. The sample was further selected for doping of silver ions.

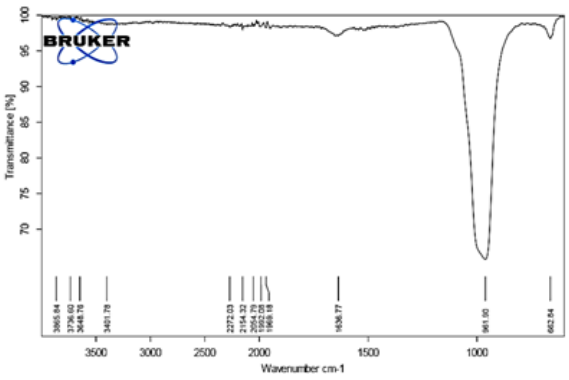

Fig. 1 Infrared Spectroscopy of CA based MS 4A sample

3.2 Preparation of Silver Exchanged MS 4A

150 ml of 0.01N of $AgNO_3$ solution was prepared and 2.5g of MS 4A powder was placed in a conical flask, stirred with the help of laboratory shaker for 30

minutes at room temperature. The pH during agitation was maintained about 6 ± 0.2 to attain the maximum exchange of silver ions. Later with the help of microporous filter paper, the residual mass was separated by using vacuum pump and oven dried for 12h at 60 ºC. The same methodology was adopted to prepare silver exchanged CA based MS 4A samples by

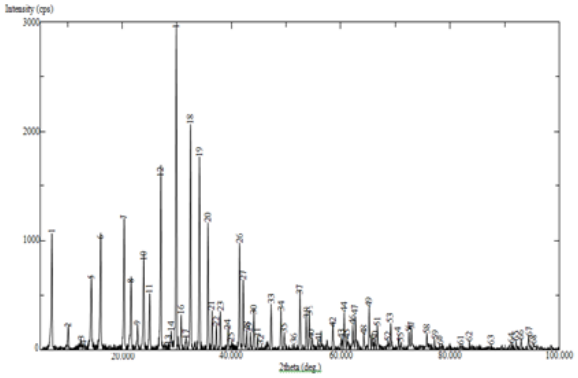

Fig. 2 X-ray Diffractogram of CA based MS 4A sample

varying the concentration of $AgNO_3$ solution (0.1 to 0.001N) to optimised the doping of silver ions in order to study the anti-microbial activity.

3.3 Evaluation of Antimicrobial Activity of Ag Exchanged CAMS 4A

Agar Well Diffusion method was employed for the evaluation of antimicrobial activity of Ag-MS 4A sample reported elsewhere **[34]**. Ag-MS 4A ranging in concentration from 0.001 N to 0.1 N was subjected to the tests with gram- negative bacteria E-coli. Experiments were carried out at Rajiv Gandhi Biotechnology Centre, Nagpur University. Results are expressed as the width of region of depletion created for the growth of bacteria. Control assays were also performed in absence of zeolites. Results are elaborated in **Table 2**.

Table 2: Reaction Strictures for Ag-Ca Ms 4a

Sample ID	Normality of AgNO3	Shaking Time (min)	Depletion Region (cm)
CA MS 4A	-	-	0.1
Ag-CA MS 4A 1	0.1	27	1.9
Ag-CA MS 4A 2	0.01	27	1.8
Ag-CA MS 4A 3	0.001	27	0.8

IV. CHARACTERIZATIONS

Fourier Transform Infrared Spectroscopy was performed to study the bare bone structure of MS 4A sample before and after doping of silver. The schematic investigation of this framework structure falls under the range of wave number 400-4000cm^{-1}. The infrared spectra of CA based MS 4A and Silver doped MS 4A were recorded on Bruker apparatus. The comparative Infrared spectroscopic analysis of CA based MS 4A with Silver doped MS 4A sample has been reported in **Figure 3**. The Crystallinity of pre and post MS 4A samples along with identification of silver ions was monitored using X-Ray Diffraction method and the diffractograms are depicted in **Figure 4.** The X-ray diffraction patterns of both the samples were recorded at 2θ values between 5° and 60° obtained using an X-ray diffractometer (Philips PAN Expert- pro) with Cu-K alpha radiation at 40Kv and 30 mA. The change in structural morphology due to doping of silver ion on MS 4A samples was obtained by Scanning Electron Microscopy (SUPRA 40)and the micrographs of both the samples are recorded as depicted in **Figure 5.**

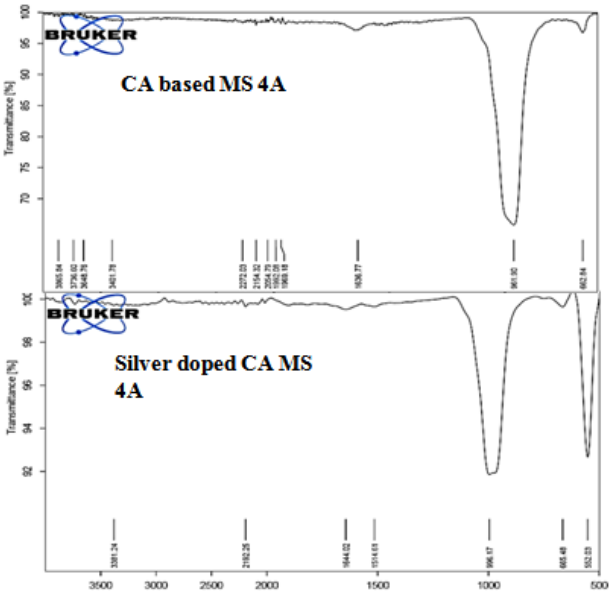

Fig. 3 Infrared spectrograms of CA based MS 4A and silver doped MS 4A

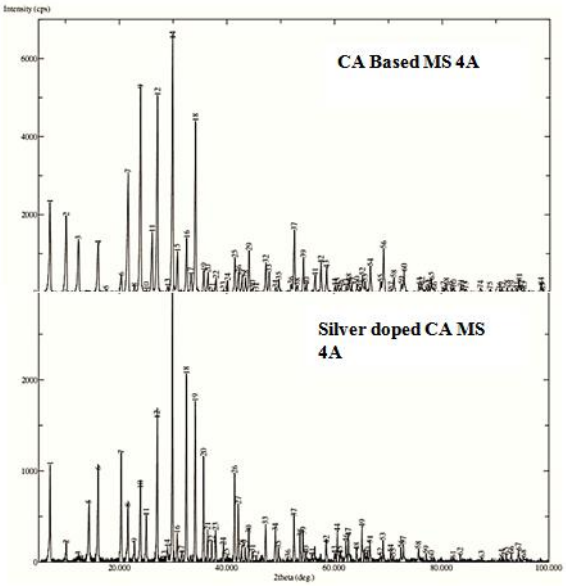

Fig. 4 Comparative study of X-ray diffractograms of CA based MS 4A and silver doped MS 4A

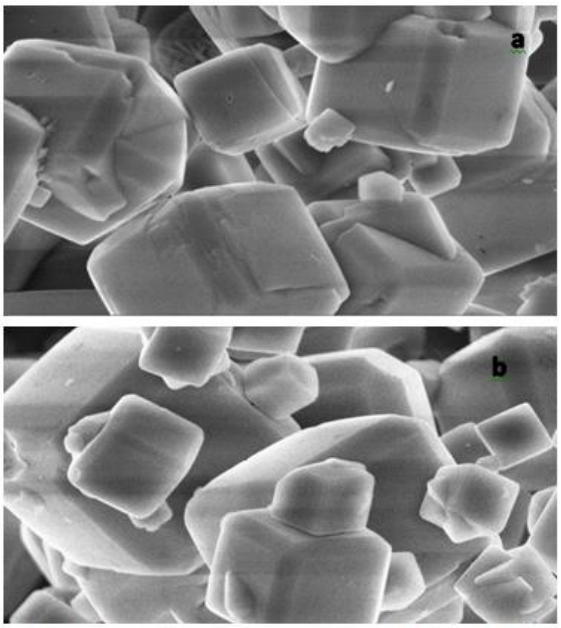

Fig. 5 Comparative scanning electron micrographs of CA based MS 4A (a) and silver doped CA MS 4A (b)

V. RESULTS AND DISCUSSION

5.1 Shortlisting of best sample

It can be outlined from Table 1 that the CBC value of CAMS 4A-5 sample is about 508 mEq/100g; which is quite competent with commercial standard showing up to 530 mEq/100g. Further the crystallinity of same has been calculated on the basis of d-spacing values corresponding to their relative intensities of strong peaks. The sample was further evaluated with the XRD and percent crystallinity was found to be fairy matching with commercial standard. The structural built up of the sample was also carried out using FTIR spectroscopy. The IR Spectrum is witnessing typical Si-O-Si, Si-O & Al-O asymmetric stretching in the region of 1000-980cm^{-1}. Also, the weak bands at 460-480 cm^{-1} region is assigned to a Si-O or Al-O bending mode (T-O_4). Similarly, the prominent peak obtained at 650-500 cm^{-1} is indicating the presence of double rings, D4R in MS 4A structure. The broad band observed at 3400-3500 cm^{-1} is characteristic of hydrogen (OH) bonded to oxygen ions and the peak at 1630-1640cm^{-1} predicts the characteristic of the bending mode in the water molecule as well hence shortlisted for silver doping using ion- exchange method.

5.2 Instrumental investigations of pre and post silver treated CAMS 4A-5 sample

5.2.1 Fourier Transform Infrared Spectroscopy

From the FTIR spectrogram, the peak at 552.03 cm^{-1} can be observed to be extended; which is indicating the presence of silver ions. Meanwhile the transmittance of prominent peak obtained between 650-500 cm^{-1} is observed to be reduced verifying that Structural framework changes up to certain degree of extent.

5.2.2 X-Ray Diffraction

The evidence of silver ions loaded in the voids of on MS 4A structure was recorded during careful examinations of X-ray diffractograms of pre and silver exchange MS 4A sample. The presence of peaks in diffractogram of silver exchanged MS 4A sample, at corresponding 2θ values of 37.960°, 44.1°, 65.220° and 75.740° are attributed to the existence of silver ions in trace amount (Ref. 01-087-0717 of JCPDS).Intensities of small peaks are observed to be reduced probably due to doping of silver ions at surface along with interior of crystal structure of MS 4A.

5.2.3 Scanning Electron Microscopy

The Scanning Electron Micrographs of bare as well as silver doped CA based MS 4A samples depict well developed cubic structure. However, the expected changes in the micrograph of silver doped sample were not observed significantly. The plausible explanation for the same could be the mild concentration of silver ions (0.01 N) applied for doping upon MS 4A surface to retain its economic viability. Minor changes in cubical morphology of both the samples may be attributed to the amorphous phase region of MS 4A.

5.3 Investigation of Antimicrobial Activity of Ag-MS 4A

Comparative investigation of pre silver exchanged CA MS 4A 5 sample has been conducted

and the results are presented in **Figure 6.**Form the picture itis evident that there is no substantial microbial inhibitory activity towards E-coli. However, the Ag doped CA based MS 4A sample exhibiting remarkable antimicrobial properties. It is deduced from the results that the antimicrobial activity is enhanced with the increase in doping concentration of $AgNO_3$ salt from 0.001 to 0.1N. Infact, it is also noted that the antimicrobial activity observed with 0.1 N and 0.01N was quite comparable i.e. 1.9 cm and 1.8 cm respectively. The optimised sample (0.01 N) exhibiting the repellence up to 1.8 cm which is considerably higher by 50% the value previously reported in literature **[35].** Hence CA based MS 4A doped with the concentration of 0.01 N $AgNO_3$ solution is identified as best sample showing maximum region of depletion.

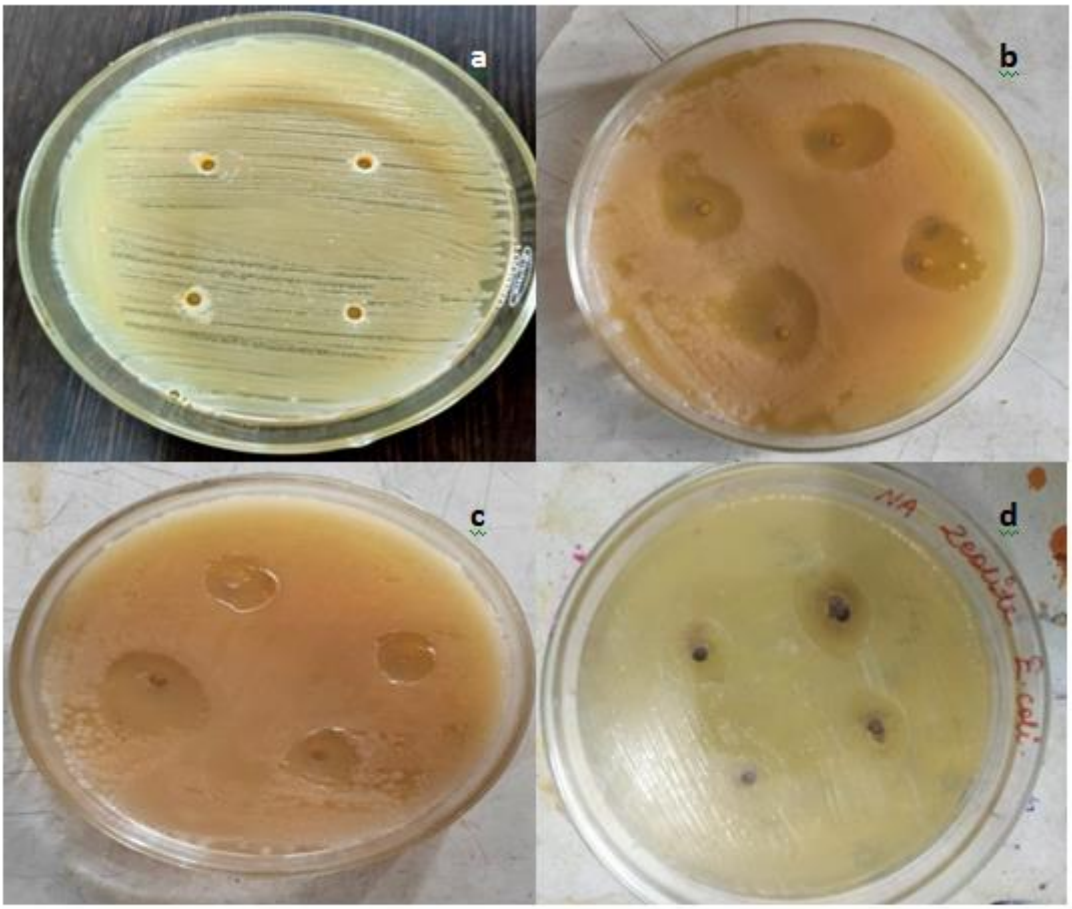

Fig. 6 Antimicrobial Activity assays in absence of silver ions (a), with 0.1 N (b) with 0.01 N (c) and with 0.001 N (d) $AgNO_3$ solutions respectively

VI. CONCLUSIONS

Easy, non-tedious and eco-friendly steps have been followed during overall process. Whereas the hydrogen gas liberated during the intermediate step for the synthesis of MS 4A is the additional utility for the process. Further, on the basis of analytical characterizations of MS 4A sample produced using composite ash has proven promising to great extent compared with commercial standard. The most promising sample was shortlisted and selected for silver ion doping to inculcate antimicrobial activity. The optimum concentration of silver ions has been deduced on the basis of repellence activity against E-coli. The antimicrobial properties explored due to doping of silver ion on MS 4A framework indicate the potential of our sample as an antimicrobial agent in food industries as well as water and wastewater treatment.

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Author Conflict of Interest Statement

We declare that the manuscript is original, has not been published before and is not currently being considered for publication elsewhere. Further, we wished to confirm that there are no conflicts of interests associated with this publication. The manuscripts have been read and approved by all the authors.

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