

Advantages of nano-silver-carbon covered alumina catalyst prepared by electro-chemical method for drinking water purification

V. Shashikala^a, V. Siva Kumar^a, A.H. Padmasri^a, B. David Raju^a,
S. Venkata Mohan^b, P. Nageswara Sarma^b, K.S. Rama Rao^{a,*}

^a *Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500007, India*

^b *Bio-Environmental Engineering Centre, Indian Institute of Chemical Technology, Hyderabad 500007, India*

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Abstract

The present work highlights the high efficiency of silver nano-particles deposited over carbon covered alumina (CCA), by electro-chemical deposition method over impregnation method, in controlling microorganisms in water. The anti-microbial activities of the catalysts are determined quantitatively by serial dilution followed by inoculation method. The catalytic characterization of these materials obtained by using transmission electron microscopy (TEM), X-ray diffraction (XRD) and temperature programmed reduction (TPR). TEM and X-ray line broadening technique results indicate the presence of Ag particles in nanometer size. The main advantage of Ag supported catalysts prepared by electro-chemical deposition over that made by conventional impregnation technique is that only small amount is needed and no pretreatment conditions like reduction are required for deactivation of microorganism in water. Thus, silver catalysts prepared by this method are not only efficient but also economical in restoring hydrogen economy. The combined characteristics of Al₂O₃ and carbon like low acidity, high mechanical strength and presence of meso pores in CCA are also helpful for getting good activity.

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1. Introduction

Pollution crisis is a major problem all around the world. It has adversely affected the lives of millions of people and caused many deaths and health disorders. Water pollution is one of the main causes for this crisis and majority of the water-borne diseases are spreading because of the poor quality of water, particularly due to the presence of bacteria and viruses in the water. Hence, it is utmost important to purify water before its use as it is one of the basic needs for the existence of mankind. There are several methods of water purification like chlorination [1], iodination [2,3], ozonation [4], UV-purification [1], reverse osmosis [5] and using silver catalysts [6]. Chemical purification like adding chlorine or iodine or applying ozone to kill the bacteria has several disadvantages, for example, excess chlorination could lead to cancer. Other methods like UV-purification and

reverse osmosis are not cost effective. Ever since silver has been recognized as an anti-bactericide, its application in purification of water is increasing.

It has been reported that the use of silver may be linked to man's earliest attempts to improve his environment. Silver vessels have been used since ancient times to keep water, wine and vinegar for purification and the anti-bacterial action of silver is due to the fact that metallic silver is said to dissolve in water in about 10⁻⁵ g/l which is toxic to *E. coli* and *Bacillus typhosus*, both of which can cause virulent diseases. Two thousand and five hundred-year long history of the use of silver for water purification and disease control has been established with no reports of toxic reactions to the hundreds of millions of children and adults exposed to it.

Heinig developed a catalytic cartridge-containing layer of silver micro-crystals deposited on α -alumina and showed that lightly bound nascent oxygen on micro-crystals of silver readily oxidizes bacteria or viruses and completely disintegrates them [7]. The anti-bacterial and antibiotic actions of silver compounds are reported in literature [8–10]. The catalytic oxidation

* Corresponding author. Tel.: +91 40 27160123; fax: +91 40 27160921.
E-mail address: ksramarao@iict.res.in (K.S. Rama Rao).

by the metallic silver on the walls of the container as well as reaction with the dissolved monovalent silver ion probably contributes to the bactericidal effect of silver vessels [11]. Supported silver catalysts are reported to be effective in deactivating microorganism [12]. Antelman in his research indicated that in an aqueous medium the peroxide Ag(III) works about 240 times as fast as Ag(I) and is up to 200 times more effective a disinfectant than Ag(I) compounds or metallic silver [13]. Electrically driven silver ions are reported to overcome a critical problem in the treatment of serious bone infections [14] and severely burned hands and fingers [15]. Resin loaded with silver ions is used to disinfect and/or remove iodine from water [16].

Hydrogen is the latest in the succession of energy providers, with many social, economic, and environmental benefits to its credit including its utilization in chemical industries which accounts for 40% of its consumption. This implicates the preciousness of H₂ and its high demand to the world today and tomorrow. Considerable amounts of hydrogen is being consumed in the various reduction processes, namely reduction of metal catalysts that are employed for various hydrogenation and other reactions apart from its usage in the hydrogenation reactions itself. Thus, preparation methods that can produce catalysts directly in metallic form without employing any hydrogen for bringing the oxidic or other forms of catalysts to their metallic forms can be highly advantageous in reducing hydrogen consumption. The present work is an endeavor in this process of maintaining hydrogen economy by synthesizing nano-metallic particles of silver employing novel electro-chemical deposition method over carbon covered alumina support. This method gives a silver catalyst, which is highly efficient in controlling microbes in water.

2. Experimental

2.1. Preparation of catalysts

2.1.1. Preparation of carbon-covered alumina (CCA)

About 5 g of γ -alumina, Al-1116E (M/s. Harshaw Chemical Co. England) sieved to 18/20 BSS mesh particle size was taken into a Quartz reactor by setting a bed with Quartz wool. N₂ is bubbled through a reservoir containing cyclohexene and the vapors were pyrolysed on γ -Al₂O₃ kept at 873 K for 6 h to get carbon covered alumina (CCA).

2.1.2. Preparation of CCA supported silver catalyst by electro-deposition method

The silver solution was firstly generated by passing low but constant dc voltage electricity (40 V) through the silver electrodes (0.4 mm thickness and 10 mm width and 100 mm long plates) immersed in distilled water. This solution was then used to test the presence of microorganism activity in the water samples. The AgCCA catalysts by electro-chemical deposition method which are designated as AgCCA-EC, respectively, were prepared by taking requisite amounts of CCA in distilled water and silver particles were generated by the above method while maintaining a constant rapid stirring for a calculated amount of

time so as to obtain a 2 wt.% of Ag in the final catalyst. The excess water was then evaporated over a hot plate followed by drying in an oven at 383 K for 12 h.

2.1.3. Preparation of CCA supported silver catalyst by impregnation technique

Conventional impregnation technique was adopted to prepare silver on carbon covered alumina catalyst. To an aqueous solution containing requisite amount of silver nitrate, previously prepared CCA support of known weight to obtain 2 wt.% was added and kept for stirring for 1 h followed by removing the excess water by evaporating on a hot plate with stirring and drying in a hot air oven for over night. The dried samples were then reduced in a flow of hydrogen at 523 K for 3 h. This catalyst was termed as AgCCA-IMP.

2.2. Characterization of catalysts

2.2.1. Transmission electron microscopy (TEM)

This technique was used to find out the range of Ag particle sizes obtained after depositions of silver particles on support CCA, both in conventional and electro-chemical method. This was done with the help of transmission electron microscopy (TEM) (M/s. Philips, Netherlands, Model: Tecnai Feil2, capacity: 120 KV). Samples were prepared by sonicating the finely powdered catalysts in methanol for about 15 min. Samples thus prepared were placed on sample holders made with gold.

2.2.2. Powder X-ray diffraction (XRD)

The XRD patterns of reduced samples of AgCCA-IMP and dried samples of AgCCA-EC were recorded on a Rigaku Mini-flex X-ray diffractometer (M/s. Rigaku Corporation, Japan) using Ni filtered Cu K α radiation adjusting 2 θ ranging 2° to 80° and with 2 θ scan speed of 2°/min.

2.2.3. Temperature programmed reduction (TPR)

TPR patterns of dried samples of support CCA, AgCCA-IMP and AgCCA-EC were obtained using a home made on-line quartz microreactor interfaced to a thermal conductivity detector (TCD) which in turn was connected to a data station (comprising of a standard GC-software supplied by Hindetron, India) for recording the profiles. H₂/Ar (6 vol.% of H₂ and balance Ar) mixture was used as the reducing gas at a heating ramp of 5 K/min from 303 to 973 K and kept at the final temperature isothermally for 30 min. The experimental details of the TPR run were discussed elsewhere [17].

2.3. Activity test

Activities of silver catalysts were tested by immersing different amounts of catalysts, viz., 0.1, 0.2 and 0.5 g each of AgC-EC, AgC-IMP, AgCCA-EC and AgCCA-IMP in 50 ml of raw water (pond water, which contains plenty of microorganisms with *E. coli* as main bacterial type present) taken in a 100 ml sterile, transparent vessel with screw cap and stirred for 1 h in a batch mode at room temperature. After 1 h, the catalyst was filtered

off and the water was tested for the presence of bacteria quantitatively.

2.3.1. Quantitative analysis of microorganisms

Raw water to be analyzed was taken and serially diluted [18] to 10^{-6} dilution in a series of six test tubes. One millilitre of the raw water was taken in the first test tube containing 9 ml of saline solution and from it 1 ml was taken into the second test tube also containing 9 ml of saline solution. This process is repeated to the last, i.e., 10^{-6} dilution. Since the raw water contains large number of microorganisms, which cannot be counted, it is necessary to dilute it. From each test tube 0.1 ml of water was taken and was spread using a spreader, on a Petri-plate containing solidified nutrient agar and were incubated at 310 K for 24 h [18]. This entire process was done in the UV laminar airflow. The number of colonies grown were then counted after incubation. This process was performed around 16 batches using variable amounts of catalysts, viz., 0.1, 0.2 and 0.5 g each of AgC-EC, AgC-IMP, AgCCA-EC and AgCCA-IMP, respectively. The quantification of microorganisms in the water was done after vigorous stirring of about 50 ml of raw water with the catalyst taken and after filtering off the catalyst. The details of preparation and characteristics of AgC-EC and AgC-IMP were reported earlier [19].

2.3.2. Nutrient agar preparation

Twenty-eight grams of nutrient agar was dissolved in 1000 ml of water and was autoclaved at 394 K and at a pressure of 15 lbs for around 15 min, samples were taken out after reducing the pressure to atmospheric pressure. Then after cooling it was distributed in 36 Petri-plates with 5 ml in each Petri-plate and left for solidification.

2.3.3. Preparation of the saline solution (0.96 wt.%) and plating

2.88 g of NaCl was dissolved in 300 ml of distilled water. Nine millilitres of this saline solution was distributed in 30 test tubes. They are covered with a cotton plug and were autoclaved same as above. They were then cooled and inoculated [18]. 0.1 ml of the inoculated culture from these test tubes was taken and spread on the agar Petri-plates for quantification of microorganisms. Thus, prepared agar plates were incubated [18] for 24 h at a temperature of 310 K.

2.3.4. Regeneration of the catalyst

After using for the first batch to control the bacteria in water the Ag supported on carbon and carbon covered alumina catalysts prepared in electro-chemical method were filtered and dried in hot air oven for overnight at 393 K and used for the next batch to test their activity in controlling microorganisms.

3. Results and discussion

3.1. XRD results

Fig. 1 depicts the XRD patterns of AgCCA catalysts, i.e., AgCCA-EC (dried) and AgCCA-IMP (reduced), respectively. The XRD pattern of impregnated Ag over active CCA is recorded

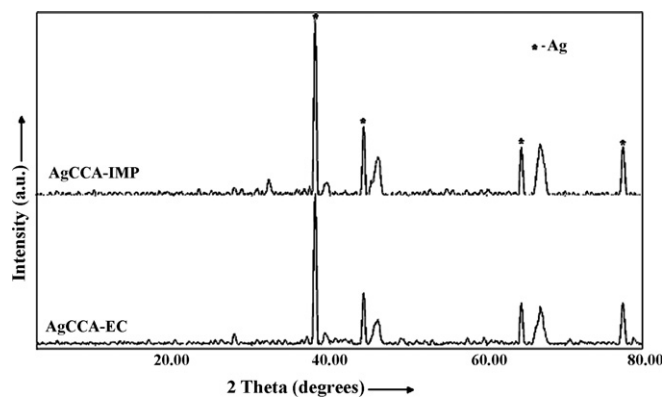


Fig. 1. XRD patterns of AgCCA-EC and AgCCA-IMP catalysts.

for the reduced form of the catalyst where as the XRD pattern for the catalyst prepared by electro-chemical deposition method is of the dried form. The catalysts showed amorphous carbon phase and silver in metallic phase [Ag with d values 2.36_x, 2.04₄, 1.25₃—ASTM card no. 4-783]. The pattern AgCCA-EC clearly show that the dried form of the catalyst itself is in metallic form and thus need not be reduced any more. On the other hand, the impregnated catalysts have to be reduced in H₂ flow for at least 2 h at 523 K to get the metallic phase of Ag.

Particle size of the silver particles in AgCCA-EC and AgCCA-IMP catalysts, calculated from the X-ray line broadening (XLB) shows nearly same particle size in both cases. AgCCA-EC has the silver with average particle size ~25 nm and AgCCA-IMP has the silver with average particle size ~27 nm. This is also confirmed from the TEM results.

3.2. TPR results

Fig. 2 shows TPR pattern of support CCA, dried catalysts of AgCCA-EC and AgCCA-IMP, which are prepared by electro-chemical and conventional methods, respectively. The TPR pattern of AgCCA-EC catalyst exhibit only a single reduction peak centered at T_{max} of 760 K that is also observed in TPR pattern of the other catalyst, i.e., AgCCA-IMP. This signal may be

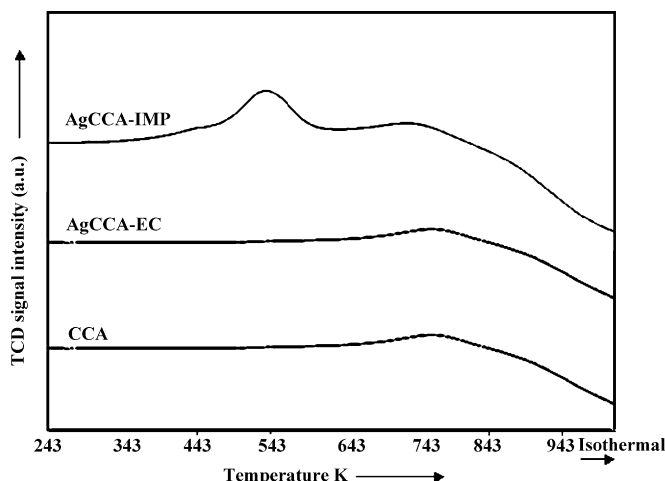
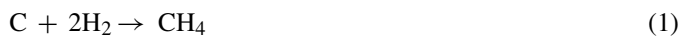
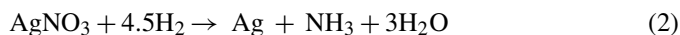


Fig. 2. Temperature programmed reduction profiles of supported silver catalysts.

attributed to the carbon-gasification of the support carbon covered alumina. The reaction of carbon with hydrogen resulting in the formation of methane was confirmed by the coupled FID analysis technique [20]. Carbon gasification can be represented as follows:



No other peaks corresponding to reduction of oxidic species of Ag is observed in the TPR pattern of AgCCA-EC catalyst. This clearly suggests that silver is already in the metallic form in this catalyst. The TPR pattern of conventionally prepared Ag catalyst showed a low temperature reduction peaks centered at T_{max} of ~ 540 K. This reduction signal is originated due to the reduction of Ag precursors, possibly either the reduction of AgNO_3 precursor or the reduction of Ag_2O . It is reported in the H_2 -TPR carried out on silver catalysts pretreated in oxygen below 373 K after reduction at 773 K for 2 h to have observed the existence of three peaks at 353, 413 and 733 K [21]. They attributed it due to molecularly adsorbed oxygen, to surface adsorbed atomic oxygen and the high temperature one assigned to the bulk-dissolved oxygen, which is the most difficult one to be reduced, respectively. It was shown in the TPR patterns of Ag/Ti fresh samples, that a broad and asymmetric peak at $T_{\text{max}} = 383$ K is ascribed to the reduction of oxygen species on finely dispersed silver and to the reduction of Ag_2O [22]. Based on these reports, it seems that the reduction signal observed in the TPR pattern of AgCCA-IMP sample in this study correspond to the reduction of AgNO_3 precursor.



Comparison of the TPR pattern of the Ag catalysts prepared by two methods with the TPR pattern of the support CCA reveals that the TPR pattern of AgCCA-EC is almost similar to that of the support with only one peak of carbon gasification and that of AgCCA-IMP shows the silver nitrate reduction peak in addition to the carbon gasification. This clearly indicate that the silver is in metallic form in AgCCA-EC catalysts, which is not the case with the impregnated catalyst.

For controlling the microorganisms in raw water, it is assumed that silver should be in metallic form so that it can take dissolved oxygen from water. Thus, for the catalyst AgCCA-EC, no pretreatment is needed for controlling the microorganisms in water. Whereas the silver catalyst prepared by conventional impregnation technique requires reduction prior to use in controlling microorganisms in water because silver is in ionic form and also AgNO_3 precursor in the catalyst may leach into the water there by causing depletion of concentration of silver in the catalyst.

3.3. TEM results

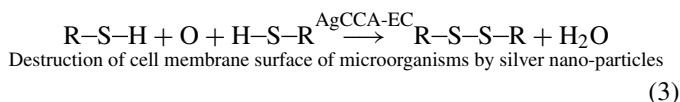
Fig. 3 shows transmission electron micrographs of CCA, AgCCA-IMP (reduced) and AgCCA-EC catalyst used for testing the microbial inhibition activity in water. The figure indicates the presence of the silver in nano-particles range. Particles are more uniformly distributed in electro-chemical method com-

pared to the conventional impregnation method. Silver particles are clearly seen in both catalysts prepared in impregnated and electro-chemical methods, when compared to electron micrograph of the support CCA.

3.4. Catalytic activity of silver on microorganisms

A report discusses three mechanisms of deactivation that silver utilizes to incapacitate disease-causing organisms [23]. They are catalytic oxidation, reaction with cell membranes, and binding with the DNA of disease organisms to prevent unwinding. Among all the metals, silver is unique in its affinity towards oxygen. It is reported that atomic oxygen has an almost perfect fit in the octahedral holes of gold, silver and copper. However, in gold the electron cloud of oxygen tends to be expelled by lattice oxygen of gold atoms and this blocks the movement through holes. Copper, on the other hand, forms the oxide providing an impossible barrier. Silver offers so little repulsion to oxygen that only a small amount of thermal energy is required to readily move the atomic oxygen through the silver lattice [24].

Micro-crystals of silver have a tendency to lightly bound nascent oxygen (with a binding energy of only 40 kcal/mol) and these species readily oxidizes bacteria or viruses, resulting in complete disintegration [7]. Silver in its atomic state, has the capacity to absorb oxygen and act as a catalyst to bring about oxidation. Because oxygen is more electronegative than sulfur, atomic (nascent) oxygen absorbed onto the surface of silver ions in solution will readily react with hydrogen attached to sulfur in the sulfhydryl ($-\text{S}-\text{H}$) groups surrounding the surface of bacteria or viruses. The removal of hydrogen atoms (as water) causes the sulfur atoms to condense to form a $\text{R}-\text{S}-\text{S}-\text{R}$ bond; blocking respiration and causing the bacteria to expire.



There are many forms of silver, viz., silver salts, organic precursors of silver, metallic form of silver on carbon, which may exhibit microscopic particle size and show germicidal, antibiotic and other effects, but are not always found to be safe and are less effective than the silver generated by electro-deposition method. In the case of silver nano-particles in water solution generated by electrolytic method, ~ 30 ml of such solution is required to deactivate bacteria in a 20 ml raw water [19]. Moreover, it is very difficult to separate the Ag particles in the solution and to reuse them. Thus, this Ag solution deposited on active carbon and carbon covered alumina seems to be more advantageous particularly in reusing the catalyst. Silver particles produced by this method are ideal sized and provide the greatest biological benefit and are proved to be non-toxic as well.

3.4.1. Quantification of microorganisms

Table 1 compares the activity of AgC and AgCCA catalysts prepared in both electro-chemical method and conventional impregnation method, i.e., AgC-EC and AgCCA-EC; AgC-IMP and AgCCA-IMP, respectively. Qualitative analysis of the activ-

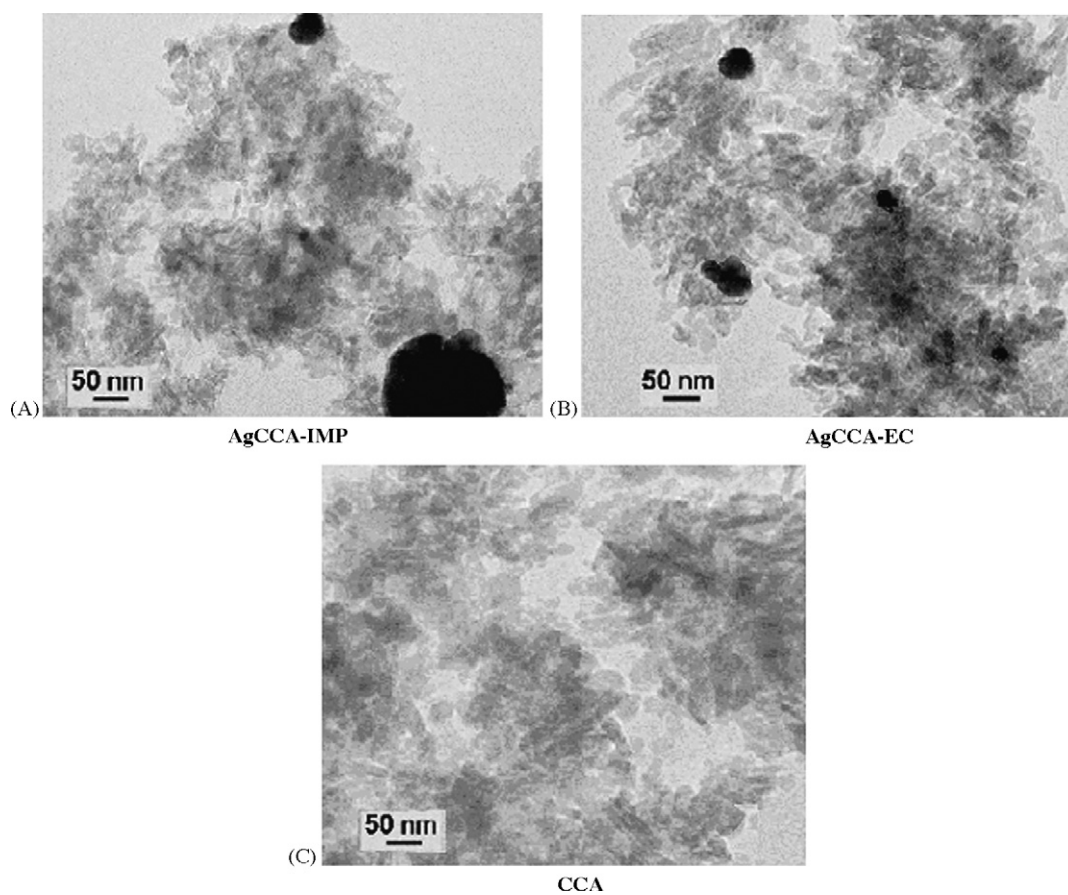


Fig. 3. TEM images of AgCCA-IMP, AgCCA-EC and CCA catalysts.

ity of both AgC-EC and AgC-IMP catalysts has been reported previously [19]. The data of quantitative analysis of microorganisms present in the water samples after treating with silver catalysts clearly indicated that the electrochemically deposited silver on active carbon and CCA are very efficient in controlling the microorganisms. The raw water, i.e., without a catalyst that is tested has shown the presence of large number of bacterial colonies that could not be counted by the method adopted in this work. Although impregnated catalysts have also shown some

efficiency in controlling the microorganisms they are efficient when taken in more amounts than electrochemically prepared catalysts. The activities of the four different catalysts studied are found to be in the decreasing order as follows:

$$\text{AgCCA-EC} > \text{AgC-EC} > \text{AgCCA-IMP} > \text{AgC-IMP}$$

Fig. 4 compares the activity profile of the four catalysts (taken in 0.1 g quantity). The activities of the Ag catalysts prepared in EC method clearly indicate the higher efficiency of AgCCA-EC or AgC-EC over the AgCCA-IMP or AgC-IMP since even 0.1 g of former catalyst is sufficient enough in controlling the microbes unlike the later, which is needed in at least 0.5 g quantity. The higher activity of AgCCA-EC or AgC-EC over AgCCA-IMP or AgC-IMP can be explained as to the formation of nano-particles of metallic Ag in the former one as observed from XRD, TPR and TEM. Also this catalyst is economical since various other steps, namely calcination and reduction in hydrogen at high temperatures are not necessary for the preparation of this catalyst.

Table 2 clearly shows the reusability of the Ag supported catalysts and their advantage over colloidal silver solution, where in the silver particles are not reusable.

Thus, it is found that Ag deposited by electro-chemical deposition is superior in controlling the microorganisms in water. The advantage of CCA over carbon lies in the combined characteristics of carbon and γ -alumina [25]. γ -Alumina has more

Table 1
Performance of AgC and AgCCA catalysts

Catalyst	Weight of the catalyst (g)	CFU count $\times 10^2$
No catalyst	–	700,000
AgC-IMP	0.1	130,000
	0.2	600
	0.5	5
AgCCA-IMP	0.1	13,000
	0.2	40
	0.5	3
AgC-EC	0.1	2,000
	0.2	0
	0.5	0
AgCCA-EC	0.1	10
	0.2	0
	0.5	0

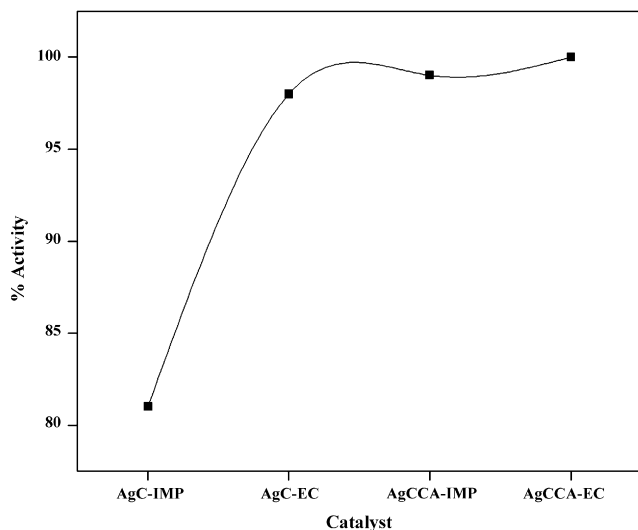


Fig. 4. Activity evaluation of catalysts with 0.1 g catalyst.

Table 2
Activity of the regenerated Ag catalysts prepared in EC method

Catalyst	Weight of the catalyst (g)	CFU count $\times 10^2$
No catalyst	–	7×10^5
AgC-EC	0.2	2
AgCCA-EC	0.2	0

mechanical strength over carbon. Hence, one can report that the mechanical strength of γ -alumina is more than that of carbon. Even though alumina is reported to be acidic, the carbon coverage on alumina (CCA) decreases the acidity of Al_2O_3 by more than 90% [26,27]. Activated carbon possesses very large surface area of the order of $\sim 1000 \text{ m}^2/\text{g}$. But most of the area comes from its micro-pores, which are not accessible for Ag particles to deposit. On the other hand, the nature of carbon in CCA is mesoporous. It is evidenced from the BET surface area of CCA ($\sim 220 \text{ m}^2/\text{g}$), which is close to that of $\gamma\text{-Al}_2\text{O}_3$ ($\sim 240 \text{ m}^2/\text{g}$). Moreover, the carbon coverage on $\gamma\text{-Al}_2\text{O}_3$ does not allow water to react directly with $\gamma\text{-Al}_2\text{O}_3$ even though this is a slow process and takes long time. Thus, the combined characteristics of $\gamma\text{-Al}_2\text{O}_3$ and carbon make CCA, a superior support for AgCCA catalyst particularly prepared by electro-chemical deposition (AgCCA-EC) method in controlling the microorganisms in water more effectively.

4. Conclusions

Electro-chemical deposition method is thus found to be novel, highly efficient in controlling the microbes. And the method of preparation is highly economical in restoring hydrogen by avoiding its use in the process of catalyst preparation, since this method yields silver directly in metallic form unlike the conventional methods of preparation of silver catalysts. It is also concluded evidently that the Ag supported catalysts are reusable. The combined characteristics of Al_2O_3 and carbon like low acidity, high mechanical strength and presence of meso pores

in CCA are also helpful for designing a highly active AgCCA catalyst.

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