

A Study on Control of Microorganisms in Drinking Water Using Ag-Cu/C Catalysts

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Abstract: Ag-Cu supported on activated carbon (Ag-Cu/C) catalysts with different compositions of Ag and Cu (total loading of Ag + Cu = 1 weight %) were prepared by wet impregnation technique. These catalysts were characterized by BET surface area XRD, TPR, TEM and XPS. The catalytic activity of these catalysts was tested for control of microorganism in drinking water by nutrient agar coating method. Catalyst containing 0.5g each of Ag and Cu respectively exhibited superior catalytic activity compared to those of remaining compositions. The high catalytic activity possessed by this catalyst is attributed to the presence of smaller Ag particles and interaction between Ag and Cu as evidenced by XRD, TPR, XPS and TEM results respectively.

Keywords: Ag-Cu/C catalysts, microorganism control, impregnation technique, water purification.

INTRODUCTION

Home owners increasingly concern about contaminants in their drinking water supply because of adverse effects on health due to the presence of bacteria and other microorganism. The presence of bacteria is the main indication of water contamination. A World Health Organization (WHO) investigation showed that 80% of disease is due to contaminated drinking water [1, 2]. The WHO recommended that any water intended for drinking should contain fecal and total coliform counts of 0 in 100mL sample [1]. To achieve this goal, chemical agents and physical treatments, such as ozone, chlorine and its derivatives, ultraviolet light and radiation, are commonly used [3]. However, these agents can easily give rise to unwanted side-effects to human health, as well as to singular events and big dosage shortcomings. The antibacterial effects of metallic silver have been known for centuries [4-6]. This beneficial property originates from silver ions dissolving from the surface of bulk silver [7]. In contrast to the use of silver ions, the biocidal effect of bulk silver is long lasting and stable. However, it is difficult to apply bulk silver in industrial or domestic applications because of its high price and low ion release rate. Recently, the application of silver nanoparticles has ushered in a new approach to the application of silver antimicrobial agents. Several investigations have been carried out to find out the bactericidal effect of nanoparticles and their applications in the plastics, health, textile, and paint industries [8-12]. In

comparison with bulk silver, silver nanoparticles release of silver ions with a controllable rate [13]. Therefore, nanoparticles are expected to play a crucial role in the food industry, water disinfection, and other applications related to disinfection [14, 15]. In our previous report silver on carbon covered alumina prepared by electrochemical deposition method has shown great potential towards purification of drinking water [16]. The objective of present work is to cut down the cost Ag/C catalyst by diluting it with Cu without compromising the activity towards microorganism control in drinking.

MATERIALS AND METHODOLOGY

Preparation of Catalysts

Commercially available activated carbon Support (M/s. Norrit Corporation, USA) has been used for silver-copper catalysts. Silver and copper are supported on activated carbon by impregnation method. Cu (NO₃)₂·3H₂O and AgNO₃ (M/s. Loba Chemie, India) are the metal precursors used for copper and silver respectively. The catalysts were prepared with varied composition of silver and copper taking increments of one metal and decrements of other metal by 0.25% by weight. Requisite amount of Ag and Cu salts are dissolved in water and the support has been dipped in this solution followed by heating to remove excess water. The resultant mass was dried in the oven for 12 hours. The samples were subjected to calcination in the flow of nitrogen (30cm³min⁻¹) at 673K for 4 hours. These catalysts were designated as 1Ag-0Cu/C, 0.75Ag-0.25Cu/C, 0.5Ag-0.5Cu/C, 0.25Ag-0.75Cu/C and 0Ag-1Cu/C which corresponds to 1% Ag, 0.75% Ag plus 0.25% Cu, 0.5% Ag plus 0.5% Cu, 0.25%Ag plus 0.75% Cu and 1% Cu by weight respectively. The compositions of all these catalysts are listed in Table 1.

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Table 1. Physico-Chemical Characteristics of the Catalysts

S. No.	Catalyst Code	Catalyst Composition, wt%		BET Surface Area		Crystallite Size, nm	
		Ag	Cu	m ² g ⁻¹ Catalyst	m ² g ⁻¹ Support	Ag	Cu
1	Carbon	0	0	912	912	-	-
2	1Ag-0Cu/C	1.0	0	765	773	68	-
3	0.75Ag-0.25Cu/C	0.75	0.25	833	841	47	-
4	0.5Ag-0.5Cu/C	0.5	0.5	775	783	38	-
5	0.25Ag-0.75Cu/C	0.25	0.75	889	898	28	-
6	0Ag-1Cu/C	0	1.0	879	888	-	-

Characterization of Catalysts

Characterization of catalysts by BET (Brunauer, Emmett and Teller) surface area, XRD, TEM, XPS and activity studies were carried out after reducing the catalysts in H₂ flow at 523K. Surface areas of the reduced Ag-Cu/C catalysts were measured by the physisorption of nitrogen at 77 K, (BET method) using a Smart Sorb 92/93 equipment (M/S.SMART Instrument, India). For the estimation of BET surface area, 30% N₂/helium gas mixture. Prior to measurement, the samples were degassed at 473K for 2h. The XRD patterns of the reduced Ag-Cu/C samples and pure carbon were recorded on a Rigaku Miniflex X-ray diffractometer (M/s. Rigaku Corporation, Japan) using Ni filtered Cu K α radiation in a 2 θ range of 2° to 80° and with 2 θ scan speed of 2°/min.

Crystallites size (L) can be determined from the corrected line broadening (β) in the sample using Debye-Scherrer equation.

$$L = k\lambda/\beta \cos\theta$$

where, θ = incident angle

λ = Wavelength

L = thickness of the crystal in a direction perpendicular to the diffracting plane.

K = constant (~ 0.9 – 1.0)

Instrumental broadening is determined by using a highly crystalline silicon standard (d = 3.1345). B is the line width on the 2 θ scale in radians, corrected for instrumental broadening as given below.

$$\beta = \sqrt{(\omega_1^2 - \omega_2^2)}$$

where, ω_1 & ω_2 are FWHM of sample & silicon standard lines respectively in the raw data..

Crystal sizes of the Ag have been calculated for the catalyst samples. However, crystallite size of Cu could not be calculated because of the poorly crystalline nature of Cu

Temperature programmed reduction (TPR) patterns of calcined samples of activated carbon support and the catalysts were obtained using a home made on-line quartz micro reactor interfaced to a thermal conductivity detector (TCD) equipped gas chromatograph (GC) which in turn was connected to a data station (comprising of a standard GC-software supplied by Hindetron, India). For recording the TPR profiles. H₂/Ar (6 vol. % of H₂ and balance Ar) mixture

was allowed to flow on to the catalyst bed and simultaneously the catalyst bed was heated at a linear ramp of 5 Kmin⁻¹ from 303 to 973K and kept at the final temperature isothermally for 30 min. H₂/Ar (6 vol. % of H₂ and balance Ar) mixture was also used as a carrier gas to the TCD equipped GC. Whenever there is a change in the concentration of H₂ from the mixture gas, due to reduction of either silver oxide or copper oxide or carbon a signal (peak) will be detected the TCD detector and these will be recorded by the GC software The experimental details of the TPR run were discussed elsewhere [17].

Transmission electron micrographs (TEM) of selected catalysts in reduced state were recorded on a Phillips Tecnai G² FEI F12 electron microscope. The powder samples were dispersed in ethanol by ultrasonication before loading onto a carbon-coated copper grid and then allowed to dry at room temperature before recording the micrographs.

XPS measurements for the selected catalysts in reduced state were performed on a Kratos X-ray photoelectron spectrometer. The X-ray excitation energy was 1253.6 eV (Mg K α), and the spectra were recorded with pass energy of 80 eV.

Activity Test

Activities of all metal supported catalysts were tested for control microorganism in raw water by using 0.1g catalyst. Prior to the activity run, the catalyst was reduced at 523K for 3h in H₂ flow (30cm³min⁻¹). Further 0.1 g of the catalyst was dipped in 50 cm³ 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.

Quantitative Analysis of Microorganisms

Water to be tested was serially diluted [18] to 10⁶ dilution in a series of six test tubes. One millilitre of the raw water was taken in the first test tube containing 9ml of saline solution and from it 1ml was taken into the second test tube also containing 9ml of saline solution. This process was repeated upto, i.e., 10⁶ dilution. Since the raw water contains large number of microorganisms, it is difficult to count the number of organisms present in it. So, 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 310K for 24 h

[18]. This entire process was done in the UV laminar airflow. The number of colonies grown was then counted after incubation. This process was performed around 16 batches using 0.1g catalysts for all Ag-Cu catalysts. 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.

Nutrient Agar Preparation

Twenty-eight grams of nutrient agar was dissolved in 1000 ml of water and was autoclaved at 394K 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 5ml in each Petri-plate and left for solidification.

Preparation of the Saline Solution (0.96 wt.%) and Plating

2.88 g of NaCl was dissolved in 300 ml of distilled water. 9 cm³ of this saline solution was distributed in 30 test tubes. They were covered with a cotton plug and were autoclaved 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 for 24 h at a temperature of 310 K [18].

RESULTS AND DISCUSSION

Catalyst Characterization

Adsorption studies of N₂ gas onto the samples gives information about the change in the surface area of the carbon support due to the deposition Ag or Cu or both by impregnation method. Surface area values of the support and Ag-Cu supported catalysts are shown in Table 1. Surface area of the support has exhibited the major decrease when Ag particles are deposited on the support. The factors that decide the surface area of the catalyst are pore blockage and the presence of nano particles of Ag or Cu or both, in the sample. It is interesting to observe that in Cu rich catalysts (0Ag-1Cu/C and 0.25Ag-0.75Cu/C), the surface area is more or less same as that of pure support. This can be further evidenced from the surface area value per gram support (Surface area of the catalyst divided by total metal content (0.99) in 1 g catalyst). In other words, the metal content of 0.01 g is excluded; surface area due to support contribution is resulted. Since this value in the catalysts, 0Ag-1Cu/C and 0.25Ag-0.75Cu/C is close to that of pure support, one can say the absence of pore blockage due to Cu. This is a clear indication of absence of pore blockage in carbon by copper particles. This is possible when copper particles of porous structure or very small particles of Cu are present. From the above data, one can believe that pore blockage by Ag is more significant than Cu.

Fig. (1) shows the XRD pattern of activated carbon supported silver-copper catalysts. It is evident from the patterns that silver is in the crystalline state and that copper is in the amorphous form (size < 40Å). The support activated carbon is also in the amorphous state. The XRD patterns of the samples with 0.50 wt percent to 0.75 wt percent Ag show major d values for metallic silver phase at 2.36, 2.04, 1.44, 1.24 and 2θ values at 38.02, 44.15, 64.32, 77.33^o due to Ag

(111), Ag (200), Ag (220) and Ag (311) planes. Respectively (ICSD File No. 064997). The intensity of Ag phase is found to decrease with decrease in Ag loading. The XRD patterns of Cu rich catalysts (0.25Ag-0.75Cu/C and 0Ag-1Cu/C catalysts) show diffraction lines at a d-value of 2.0871 and at 2θ value of 43.317^o due to metallic Cu (111) plane (ICSD File No. 064699). The broad signal at a d-value of 3.3846 (2θ value of 26.310) is due to the presence of carbon (ICSD File No. 029123). The broad signal at a 2θ value of 43^o may be due to the poor crystalline nature of activated carbon. Crystallite sizes of Ag from XRD line Broadening (XLB) by using Debye - Scherrer equation (for the calculation of crystallite sizes, raw XRD data has been used) are shown in Table 1. It is clear that the crystallite size of Ag decreases with decrease in Ag loading. Because of the small intense signal due to Cu (111) plane, it is difficult to calculate the crystallite size. In 0.5Ag-0.5Cu/C catalyst, the particle size of Ag is 38 nm whereas the particle size of Cu is below the detection limit of XRD unit.

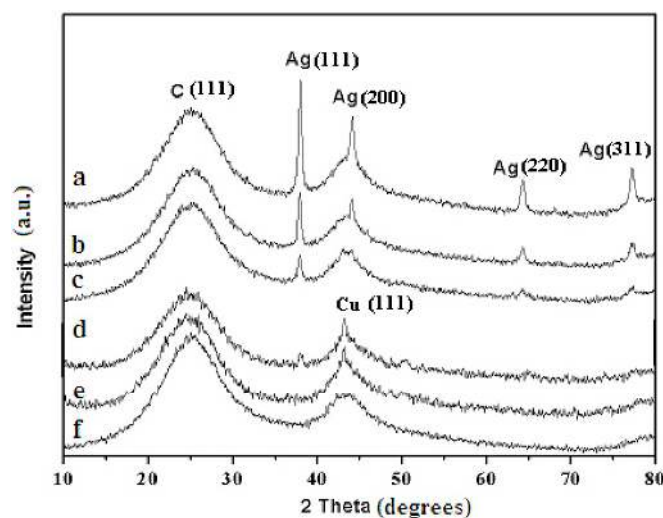


Fig. (1). X-ray powder diffraction patterns of Ag-Cu/C catalysts. (a) 1Ag-0Cu/C (b) 0.75Ag-0.25Cu/C (c) 0.5Ag-0.5Cu/C (d) 0.25Ag-0.75Cu/C (e) 0Ag-1Cu/C (f) Carbon.

Fig. (2) shows the TEM pictures of 1Ag-0Cu/C, 0.5Ag-0.5Cu/C and 0Ag-1Cu/C catalysts in reduced state. It is interesting to note that the Ag particle size in 1Ag-0Cu/C is approximately 50 nm and in 0.5Ag-0.5Cu/C catalyst is approximately 10 nm (Table 2). Particles of Cu are not visible in the TEM pictures of 0.5Ag-0.5Cu/C and 0Ag-1Cu/C catalysts. These results are in line with those obtained from XRD. Formation of nanoparticles of Ag and Cu on a high surface area support like activated carbon is not surprising when the concentration of metal content is small. In the present investigation, the total metal content is only 1% by weight and hence there is possibility of formation of Ag and Cu nanoparticles. It is reported the formation of Cu nano particles on a low surface area support like MgO, when the Cu metal content is up to 20% by weight [19-21] It is reported that silver particle size is in the nano range when Ag is deposited on activated carbon and carbon covered alumina [22, 16].

Fig. (3) shows the TPR patterns of the catalysts. TPR is one of most useful characterization technique in the area of catalysis, particularly to find out the presence of reducible

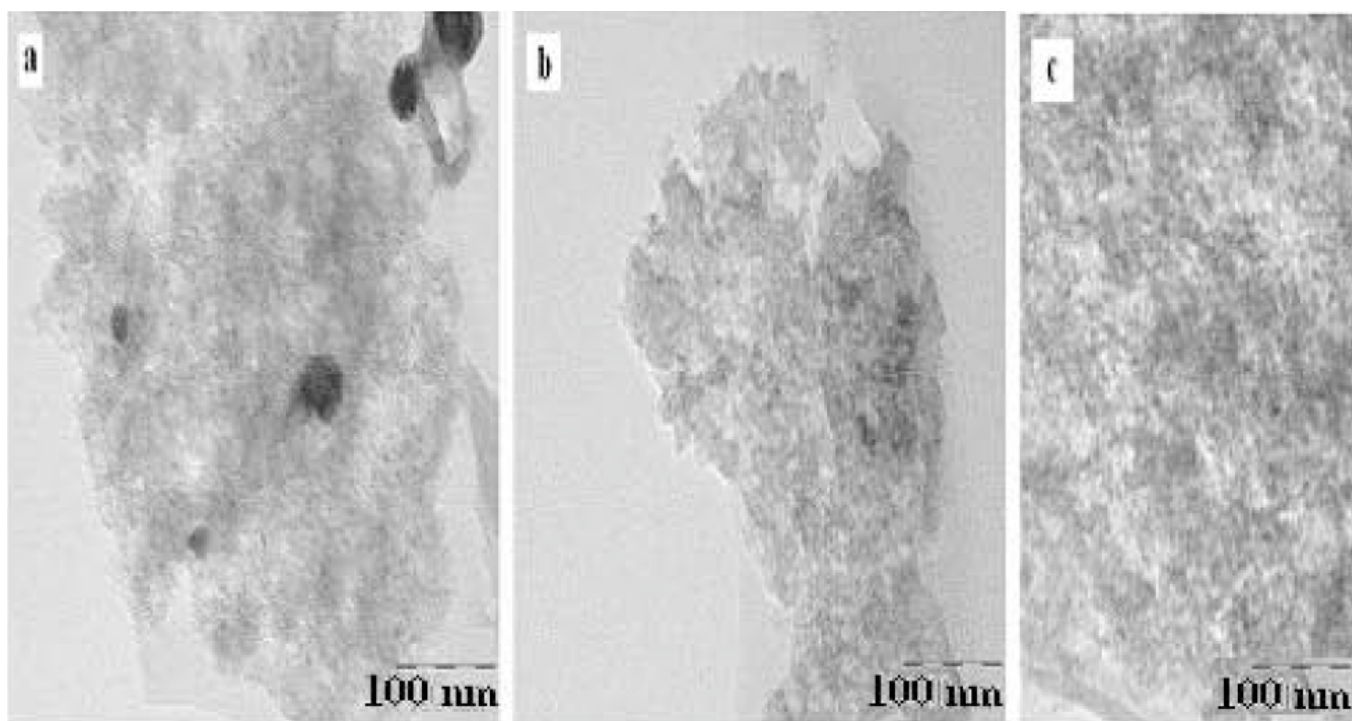


Fig. (2). TEM pictures of Ag-Cu/C catalysts. (a) 1Ag-0Cu/C (b) 0Ag-1Cu/C (c) 0.5Ag-0.5Cu/C.

Table 2. Surface Concentration and Particle Size of Ag and Cu from XPS and TEM Respectively

S. No.	Catalyst Code	Mass Concentration (XPS), wt%		Particle Size (TEM), nm	
		Ag	Cu	Ag	Cu
1	1Ag-0Cu/C	1.87	0	50	-
2	0.5Ag-0.5Cu/C	1.12	2.07	10	-
3	0Ag-1Cu/C	0	0.44	-	-

species, oxidation state of active component and the interaction between active component species. The peak significant in all the samples at around a T_{max} of 920K corresponds to gasification of carbon, where methane formation occurs.

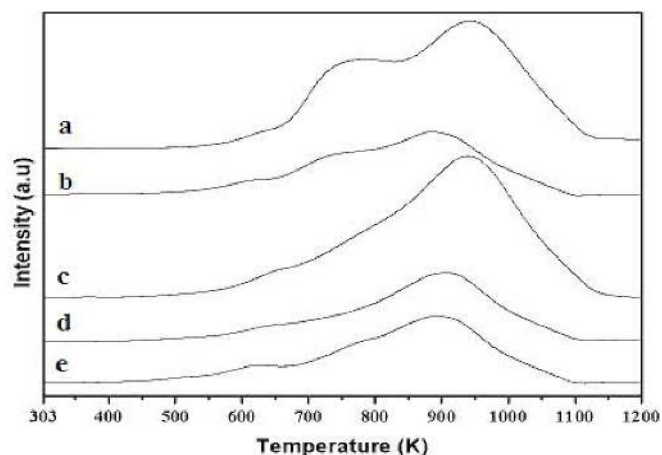
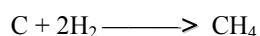
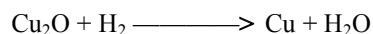


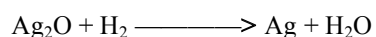
Fig. (3). TPR Patterns of Ag-Cu/C catalysts. (a) 1Ag-0Cu/C (b) 0.75Ag-0.25Cu/C (c) 0.5Ag-0.5Cu/C (d) 0.25Ag-0.75Cu/C (e) 0Ag-1Cu/C.

Carbon gasification at high temperatures beyond 750K were reported on Ag catalysts in our earlier publications [16, 22]. High temperature signal due to carbon gasification in the TPR patterns of Pd supported on carbon based supports were reported [23-28].

From the TPR pattern of 0Ag-1Cu/C catalyst (1% Cu) one can observe the reduction of carbon at relatively lower temperatures. The reduction of Cu^{+1} oxide to metallic Cu can be observed at a T_{max} of ~600K in this catalyst.



The silver oxide reduction to metallic Ag can be observed from the TPR patterns of 0.75Ag-0.25Cu/C ca, 1Ag-0Cu/C catalysts at a T_{max} of ~750K. From the TPR pattern of 0.50Ag-0.5Cu/C catalyst, it is interesting to observe a broad single peak due to the reduction of carbon and a shoulder at a T_{max} of 650K may be due the reduction of strongly interacted species or alloy formation between Cu and Ag oxides.



Thus the TPR results indicate the presence of reducible species which are present in the catalyst. In the present case, the reducible species in the catalysts are Cu_2O , Ag_2O and carbon. Since metallic silver and other coinage metals are

active in controlling the microorganism the catalysts in the oxidic form must be reduced to the corresponding metals before their application in water purification.

The XPS patterns of 1Ag-0Cu/C, 0.5Ag-0.5Cu/C and 0Ag-1Cu/C in reduced state) are shown in Fig. (4). The binding energy values of Ag $3d_{5/2}$ in 1Ag-0Cu/C and 0.5Ag-0.5Cu/C catalysts are 368.298 and 368.178 eV respectively. The binding energy values of Cu $3d_{3/2}$ in 0Ag-1Cu/C and 0.5Ag-0.5Cu/C catalysts are 932.477 and 932.344 eV respectively. The decrease of binding energy values for Ag $3d_{5/2}$ and Cu $3d_{3/2}$ in 0.5Ag-0.5Cu/C catalyst compared to those in the monometallic catalysts might be due the interaction between Ag and Cu phases. Merging of Cu and Ag oxide reduction peaks in the TPR pattern of 0.5Ag-0.5Cu catalyst confirms the formation of interacted species between Ag and Cu.

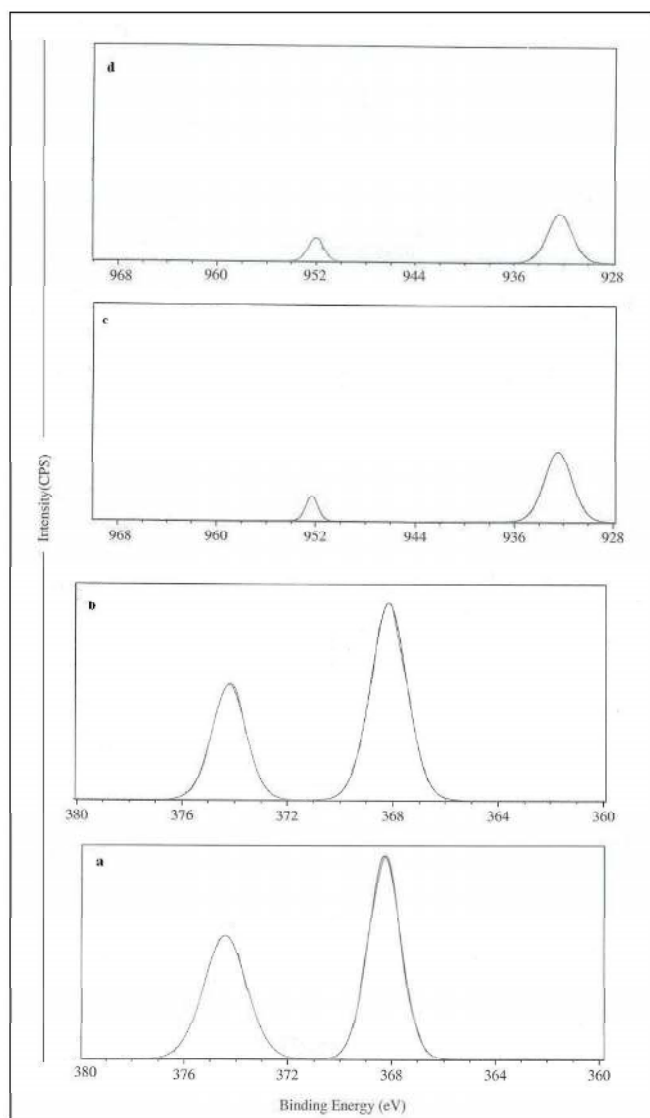


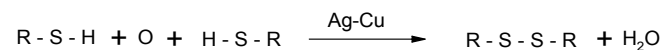
Fig. (4). XPS results of Ag-Cu/C catalysts. (a) 1Ag-0Cu/C (Ag $3d_{5/2}$ pattern) (b) 0.5Ag-0.5Cu/C (Ag $3d_{5/2}$ pattern) (c) 0Ag-1Cu/C (Cu $2p_{3/2}$ pattern) (d) 0.5Ag-0.5Cu/C (Cu $2p_{3/2}$ pattern).

Table 2 shows the surface composition and particle size of Ag and/or Cu in 1Ag-0Cu/C, 0.5Ag-0.5Cu/C and 0Ag-1Cu/C catalysts (reduced state) from the XPS and TEM data.

The surface composition of Ag (1.87%) in 1Ag-0Cu/C is more than that of Cu (0.44%) in 0Ag-1Cu/C. However, the surface composition of Ag (1.12) is lower than that of Cu (2.07) in 0.5Ag-0.5Cu/C catalyst. From this one can guess that 0.5Ag-0.5Cu/C possesses more anti microbial activity than the individual catalysts. Among the individual catalysts, 1Ag-0Cu/C expects to exhibit more anti microbial activity than that of 0Ag-1Cu/C. However, the smaller particles which are evident from the XRD and particle size from TEM (Table 2) of Cu in 0Ag-1Cu/C than that of Ag in 1Ag-0Cu/C may be a better catalyst in terms of microorganism control among the individual catalysts.

Catalytic Activity

A report discusses three mechanisms of deactivation that silver utilizes to incapacitate disease-causing organisms [29]. These are catalytic oxidation, reaction with cell membranes, and binding with 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 [30]. 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 [31]. 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 particles in solution will readily react with hydrogen attached to sulfur in the sulfhydryl (-S-H) groups surrounding the surface of bacteria or viruses. The removal of hydrogen atoms (as water) causes the sulfur atoms to condense to form R-S-S-R bond. This blocks the respiration and causing the bacteria to expire.



Quantification of Microorganisms

Raw water contains large number of colonies. After 24h incubation, the number of colonies in raw water is 125×10^6 CFU. This number goes upto to 178×10^6 CFU after 48h incubation. Fig. (5) compares the microorganism destruction ability of reduced Ag-Cu/C catalysts with various compositions of silver and copper. Both Ag and Cu catalysts are known to possess good anti bacterial activity [16, 22, 32, 33]. However in the present investigation, the catalytic activity of 0Ag-1Cu/C catalyst is more compared to that of 1Ag-0Cu/C catalyst. This is due to the smaller particle size of Cu compared to the silver particle size. No Cu particle is visible in the TEM picture of 0Ag-1Cu/C catalyst, indicating that Cu particle size is very small. On the otherhand, Ag particle size in 1Ag-0Cu/C catalyst is in the range of 50nm. XRD and TEM data supports this evidence. The data of quantitative analysis of microorganisms present in the water samples after treating with Ag-Cu catalysts

clearly indicates the highly efficient nature of 0.5Ag-0.5Cu/C catalyst towards controlling the microorganism. The raw water, i.e., without a catalyst that is tested has shown the presence of large number of bacterial colonies. Even, with activated carbon, the catalytic activity in controlling the microorganism is negligible. The high activity (nearly 80%) possessed by 0.5Ag-0.5Cu/C catalyst is due to (i) the strong interaction between Ag and Cu, (ii) presence of smaller particles of Ag and Cu and (iii) more amount surface composition of Ag and Cu.

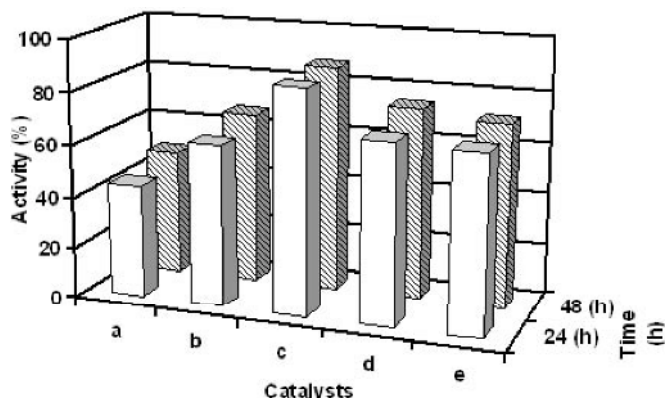


Fig. (5). Activity data of Ag-Cu/C catalysts. (a) 1Ag-0Cu/C (b) 0.75Ag-0.25Cu/C (c) 0.5Ag-0.5Cu/C (d) 0.25Ag-0.75Cu/C (e) 0Ag-1Cu/C.

CONCLUSIONS

From the activity it is clear that the best catalyst is the one with equal proportions of silver and copper, (0.5Ag-0.5Cu/C catalyst). This is due to the strong interacted species between Ag and Cu (which can be evidenced from the TPR and XPS data), the presence of smaller particles of Ag and Cu as evidenced from the XRD and TEM results and more amount surface composition of Ag and Cu. As the price of silver is costlier than copper, the diluted catalyst with equal proportions of Ag and Cu is much lower cost with higher catalytic activity towards microorganism control in drinking water.

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