Sterilization of Drinking Water By Silver Catalysts Supported on Activated Carbons

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Abstract: *Main focus of this study is to prepare high surface area activated carbons from rice straw and usage of these carbons as supports for Ag catalysts. The activated carbon UR3 showing highest surface area (1126.4 m^2g^{-1}) is used as support for preparing all silver catalysts. The catalysts are prepared in two methods impregnation method and electrochemical deposition method. All these catalysts are subjected to characterization studies such as surface area, XRD, SEM, TPR and activity studies. Catalysts prepared in electro chemical deposition method are showing high activity over the catalysts prepared in impregnation method. It is clearly observed that silver supported on carbon is more efficient in controlling microorganisms in water than the colloidal silver. Electro chemical deposition method yields smaller nano sized particles which increases the intrinsic activity and hence superior in activity compared to the catalysts prepared by conventional impregnation method. Even by using least quantity of catalyst, the microorganisms are effectively controlled which indicates the high intrinsic activity.*

Keywords: *Coliform, Electro deposition, Impregnation, Rice straw, Surface area*

I. Introduction

Catalysts play an important role in majority of chemical reactions to occur. Efficiency of the catalyst depends on its properties like surface area, porosity, acidity, basicity, crystallinity, particle size, and dispersion of the active component, number of active components, mechanical strength and thermal stability etc. [1-3]. These properties are controlled by various factors like selection of precursor and precipitating agent, pH-conditions maintained at the time of preparation, aging, concentration of solutions taken and pretreatment conditions like calcinations, reduction etc. Little change in the preparation method will alter the properties of catalysts and they affect the performance of the catalyst. Thus preparation of catalyst is the key step. There are varieties of techniques available to characterize the catalysts.

Rice straw from the agricultural industries is an abundant biomass resource in India and China that has typically been treated using traditional methods such as composting and incineration. However, they are not suitable to process this solid waste as rice straw contains small concentrations of nitrogen for composting and a considerable amount of solid grains that would generate smoke in to the environment during incineration [4]. The rich in volatiles and combustible ingredients, the rice straw can be employed as a renewable energy source. How to reuse and recycle this valuable biomass resource is a very urgent significant, yet difficult job [5]. The most explored adsorption property is observed in activated carbon which is used to remove dyes from wastewater due to its excellent adsorption ability [6]. The bio char derived from relatively low-temperature pyrolysis [7-8] and the structure of bio char derived from high temperature pyrolysis which may increase the adsorption capacity (a desirable property for an activated carbon) is explained by Lehmann et al [9]. Pyrolysis of hydrocarbons at higher temperatures under nitrogen atmosphere generates 100% pure carbon [10]. In view of value addition to rice straw, activated carbons are prepared from rice straw in different methods by Srinivas B.N. et al [11]. In the present study these activated carbons are used as supports for preparation of silver catalysts for purification of water. In earlier studies supports used for silver catalysts are commercially available active carbon and carbon covered alumina. Commercially available activated carbon contains metal and organic impurities, which are to be removed before using, by treating with acid and alkali.

The ability of silver in water purification and disease control was reported by Davies and Etris [12]. It was not until 1986 that USA Patent No. 4,608,247 was granted to C. F. Heining on the catalytic action of silver in an aqueous media for the sanitation of water [13]. Atomic oxygen adsorbed on the surface of the silver instantaneously oxidizes organic material on contact. 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. There are three mechanisms observed for silver sanitation [14]. Even though it is believed that silver deactivates 650 varieties of bacteria and viruses, some cases of bacteria

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resistance to silver has been reported by McHugh et al [15]. The list of bacteria evidences resistance to silver compounds is given by Clement and Jarrett [16]. Metallic silver is said to dissolve in water in about 10^{-5} g/L, which is toxic to E.coli and Bacillus typhousus, both of which can cause virulent diseases [17]. Developed at the Johns Hopkins University some 50 years ago, the product of Ionics, Inc., (Bridgeville, PA, USA) contains somewhat over 1% by weight of metallic silver on activated carbon with an added advantage of having activated carbon for the adsorption of organic compounds such as cancer causing trihalomethanes which may be generated by chlorine treatment in municipal water treatment systems [18]. An overview of recent progress in silver-based heterogeneous catalysts for four green chemical processes was reported by Wei-Lin Dai [19]. Recently Gosh et al [20] reported an efficient and simple technique to synthesize MSF-Ag nano composite which has been exploited to show bactericidal, antifouling and dye degradation properties in water with the object of drinking water purification. This study is focused on the use of activated carbons as supports to prepare silver catalysts for purification of water in this research investigation.

II. Experimental Methods

2.1 Materials
Rice straw was collected from Krishna district, Andhra Pradesh, India, was trimmed in to small Pieces. These pieces were soaked in 2 wt. % NaOH solution for 24 hr. to remove ash and water soluble substances. The straw was then washed with distilled water until the pH is neutral and then dried at 110^0C overnight.

2.2 Preparation of Activated Carbons
The detailed preparation methods of activated carbons was explained by Srinivas B.N. et al [11]. The supports were named as UR-0, UR-1, UR-2 and UR-3. Among all those activated carbons, the one with high surface area is used as potential support for preparation of silver catalysts.

2.3 Preparation of Silver catalysts
Silver is supported on activated carbon UR-3 prepared from rice straw supports in two methods. One is by impregnation method and the other is by electrochemical deposition method.

2.3.1 Preparation of activated carbon supported silver catalysts by impregnation method
Conventional impregnation technique is adopted to prepare silver on activated carbon as support with variable loading of Ag. To an aqueous solution containing requisite amount of silver nitrate, dried activated carbon of known weight is added and kept for stirring for 1 hour followed by removing the excess water by evaporating on a hot plate with stirring and drying in a hot air oven over night. These catalysts are termed as Ag1UR3-I, Ag2UR3-I, Ag3UR3-I, Ag4UR3-I, Ag5UR3-I and Ag6UR3-I which correspond to 1 %, 2 %, 3 %, 4 %, 5% and 6% by weight of Ag with respect to support respectively and 'I' refers to impregnation. The reason for selecting UR-3 activated carbon is due to its high surface area and pore volume. These catalysts are dried and reduced to control the microorganisms. Particle size and phase of the catalysts are studied with the help of SEM, XRD and TPR studies. The detailed results of these characterizations are discussed in the following sections.

2.3.2 Electro chemical deposition method
The Ag nano particles are generated electro-chemically by passing a D.C. current (45 V) through silver electrodes dipped in 50 ml distilled water. Activated carbon UR3 prepared from rice straw is immersed in distilled water and continuous stirring is maintained for a calculated amount of time. The water is evaporated to dryness on a hot plate with stirring and the resultant catalyst is dried in an air oven for overnight. The effect of run time (duration of passage of the current) on the size of the particles generated is examined by carrying out SEM analysis of the Ag solutions thus obtained. Based on the Ag particle size obtained from SEM analysis at different run times (presented in the following section) it can be seen that just a 5 min. time is sufficient enough to generate the Ag particles in the nano range in 50 ml water when 45v D.C. current is applied and beyond this time agglomeration of particles seem to take place producing Ag particles of bigger size. For supporting colloidal Ag on activated carbon by this method, it is assumed that the concentration of colloidal Ag is ~10 ppm. Based on this assumption a 2 wt.% of colloidal Ag deposited on activated carbon (AgUR3-E) has been prepared by suspending 5 gr. of carbon in the distilled water with vigorous stirring and the catalysts is named as 2AgUR3-E.

III. Results and Discussions

3.1 Characterization
3.1.1 BET Surface area

Surface area of all the catalysts are studied by N_2 adsorption method. The surface area of UR3 activated carbon is maximum when compared with other samples. UR3 sample has been activated at 200^0 C under air atmosphere for 2 hr. The yield of activated carbon is maximum when compared to other supports. Activation temperature and atmosphere has more influence on the yields of carbon prepared from rice straw. This influence is attributed to the difference in the strength of the precursor structure resulting from the formation of stable carbon structures during peroxidation treatment, which evaporates volatile matter and leads to opening of micropores. As porous nature increases the surface area also increases. It is interesting to see from Table-1, that the surface area of Ag1UR3-I to Ag6UR3-I catalysts decreases with increase in the percentage of impregnated silver. This indicates that the impregnated silver is blocking the pores of support and reducing surface area of the catalyst. But in 2AgUR3-E catalysts prepared by electrochemical deposition method, the surface area is increased relatively when compared with Ag2UR3-I catalyst prepared by impregnation method. The silver deposited on activated carbon by electrochemical deposition method is contributing some surface to the net uncovered support surface area.

3.1.2 X-ray diffraction studies

Fig.-1shows XRD patterns of reduced AgUR3-I catalysts prepared by conventional impregnation method. All these patterns indicate the presence of metallic silver. XRD patterns of Ag1UR3-I to Ag6UR3-I corresponds to different weight percentages of silver from 1-6 wt. % respectively, show major 'd' values for the metallic silver phase and no other Ag precursor phases are found from these patterns. The peak intensity of the Ag phase is found to increase with increase in Ag loading. In the catalyst samples containing low loadings of Ag (2 wt. %) the metallic phase is in poorly crystalline form. Fig.-1clearly shows that beyond 2-weight % Ag loading, strong intense signals due to metallic Ag can be seen. Thus, it is necessary to keep the Ag loading low in order to get smaller crystallites of Ag and to get better dispersion on support. To get smaller crystallites low loading (2 weight %) of silver is maintained in the preparation of AgUR3-E catalyst by electro-chemical deposition method.

3.1.3 SEM results

The effect of run time (duration of passage of the current) on the size of the particles generated is examined by carrying out SEM analysis of the Ag solutions, thus obtained. Table 2 presents the Ag particle size obtained from SEM analysis at different run times. It can be seen that just a 5 min. time is sufficient enough to generate the Ag particles in the nano range in 50 ml water when a 45 v D.C. current is applied. As the run time increases agglomeration of particles is observed producing Ag particles of bigger size. The SEM pictures of nano size Ag particles in water generated by electro-chemical method after a run time of 5 min. the figure clearly shows the formation of nano particles of Ag in the range of 50-180 nm. During the electrolysis run, as the size of the particle (Ag) increases, the distance between the particles decreases which results in the increase in the current (mA) (initial current of 5mA has been increased up to 10 mA). It is reported that the aqueous solution containing the silver particles (nano range) by electro-chemical method to be in the range of 10–20 ppm of Ag [21]. This catalyst is termed as AgUR3-EC. The microbial inhibition activity in water is tested with two catalysts AgUR3-I and 2AgUR3-E. Fig.2 represents the electron micrographs of these two catalysts. The figures indicate the presence of the silver as nano particles more pronouncedly seen in the electrochemical deposited catalysts.

3.1.4 Temperature Programmed Reduction (TPR) studies

Fig.3 compares TPR patterns of pure activated carbon UR-3, Ag2UR3-I prepared by impregnation method and 2AgUR3-E (2 wt. % silver) prepared by electrochemical method. A single high temperature signal centered at a Tmax of 750K in pure activated carbon UR-3 is due to the carbon gasification. In addition to the carbon gasification signal, the TPR patterns of conventionally prepared catalysts exhibit two more reduction signals, one centered around Tmax of 473K and the second one centered at a Tmax around 623 – 673K. It is reported by Gang et al [22]. This signal is observed in all the catalysts because of the gasification of carbon support. Silver catalyst prepared in electrochemical method showed only single peak at Tmax ~750 K which is corresponding to carbon gasification where as Ag2UR3-I shows a lower temperature peak at Tmax ~620 K for the reduction of silver ion to metallic silver. This indicates that nano metallic silver particles are generated during electrochemical deposition method on activated carbon support.

3.2 Activity studies

For controlling the microorganism in raw water it is assumed that silver should be in metallic form so that it can take dissolved oxygen from water. The activity of silver in controlling microorganisms is tested in

both batch and continuous flow method. Following table 3 and 4 are the results obtained in batch reaction model. Low concentration of pure silver fails to destroy coliforms in water. Table-3 clearly shows the destruction of coliforms with colloidal silver solution prepared by generation of colloidal silver particles in electrochemical method, ~30 ml such solution is required to deactivate bacteria in 20 ml raw water containing bacteria. Moreover, it is very difficult to separate these colloidal Ag particles and to reuse them. Presence of bacteria is qualitatively tested with the help of commercial Ready cult coliforms reagent. Table-4 shows the activity of the six silver catalysts (each 1 gr) with different loadings prepared in conventional method for controlling the microorganisms in water. When compared to the colloidal silver aqueous solution, Ag impregnated activated carbon supported catalysts are advantageous particularly in reduced form. All the silver impregnated activated carbon catalysts have shown antibacterial activity in raw water. However, Ag1UR3-I to Ag6UR3-I catalysts prepared by conventional impregnation technique have to be pretreated (reduction at 723 K in H_2 flow for 4 hours to get metallic silver particles on activated carbon) before their application in controlling the bacteria in raw water. Without pretreatment, there is every possibility of leaching of $AgNO_3$ into raw water thereby causing a decline in the concentration of Ag in the catalyst.

IV. Figures & tables

Table-1 Surface area of pure activated carbons and impregnated and electro deposited silver catalysts

Catalyst	S.A (m^2g^{-1})	Catalyst	S.A (m^2g^{-1})
UR0	376.0	Ag1UR3-I	1021.5
UR1	558.6	Ag2UR3-I	985.7
UR2	879.3	Ag6UR3-I	813.2
UR3	1126.4	2AgUR3-E	1064.1

Table-2 Effect of run time on the particle size of silver

Sl. No.	Voltage, V	Run time (min.)	Range of Ag particle size (nm)
1	45	5	50-180
2	45	10	100-210
3	45	15	250-800
4	45	20	750-1200

Table-3 Effect of Ag concentration in water on the destruction of coliforms

S.No.	Vol.of 10 ppm aq. Ag sol. (ml)	Vol. of raw water (ml)	Total coliforms
1	--	50	Present
2	10	40	Present
3	20	30	Present
4	30	20	Absent
5	40	10	Absent

Table-4 Biological activity of silver supported catalysts prepared in conventional method

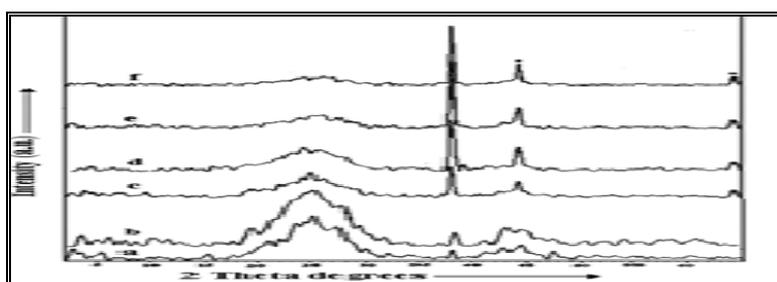| Sl.No	Catalyst Code	Volume of raw water	Total coliforms
1	----	50	Present
2	Ag1UR3-I (reduced)	50	Absent
3	Ag2UR3-I (reduced)	50	Absent
4	Ag3UR3-I (reduced)	50	Absent
5	Ag4UR3-I (reduced)	50	Absent
6	Ag5UR3-I (reduced)	50	Absent
7	Ag6UR3-I (reduced)	50	Absent

Fig.1: XRD patterns of Ag C catalysts
(a) Ag1UR3-I (b) Ag2UR3-I   (c) Ag3UR3-I (d) Ag4UR3-I (e) Ag5UR3-I (f) Ag6UR3-I
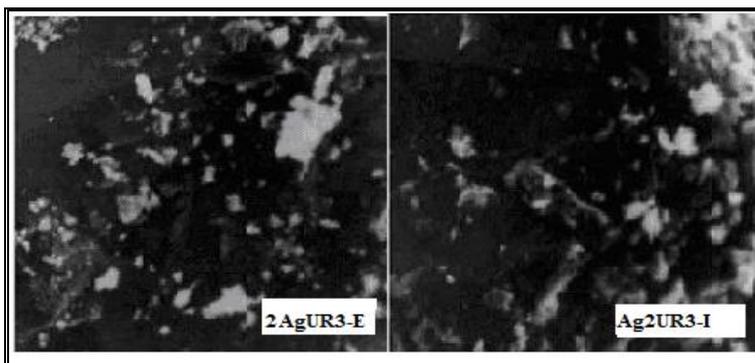
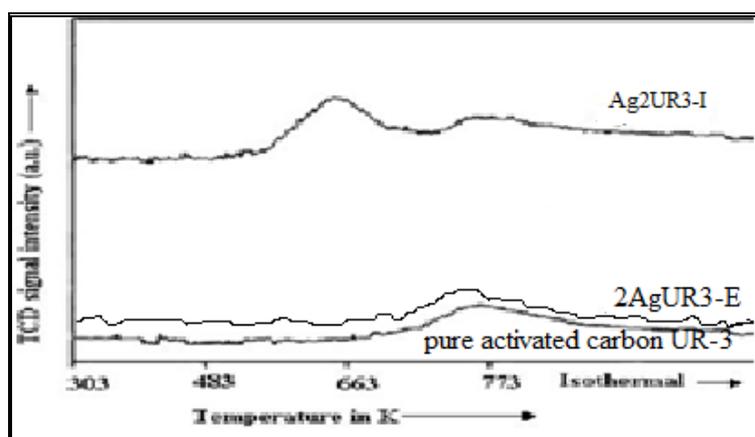**Fig.2:** SEM pictures of 2AgUR3-E & Ag2UR3-I

Fig.3: TPR patterns of pure activated carbon and silver catalysts

IV. Conclusions

The activated carbons prepared from rice straw are showing good textural properties like surface area and pore volume. Highest surface area is shown by UR3 ($1126.4 m^2 g^{-1}$) activated carbon, which is used as support for all catalyst preparations. Silver deposited catalysts by electro deposition method are showing more surface area than silver impregnated catalysts. Lower percentages of silver is showing good activity than higher percentage loading. As percentage of silver on support increases, particle size increases leading to agglomeration and pore blockage Metallic phase of silver is observed on electrodeposited silver catalysts due to which these catalysts are showing high activity in sterilization of water for removing coliform bacteria. These activated carbons were also used as supports for other metals in dehydration of alcohols [23] in our earlier studies.

Acknowledgments

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