Plasma treated activated carbon impregnated with silver nanoparticles for improved antibacterial effect in water disinfection

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ABSTRACT

A strategy to selectively attach more Ag nanoparticles on the external surface of activated carbon (AC) is being proposed and used as an antibacterial medium for water disinfection. Ag nanoparticles were first synthesized under UV irradiation by reducing silver nitrate with sodium citrate; the latter serving the dual purpose of both a reducing and a capping agent. Transmission electron micrographs show that Ag particles have a mean diameter of 28 nm with a standard deviation of 5 nm. The AC was treated by an oxygen plasma to increase the number of polar functional groups on the surface. This carbon-surface modification treatment increased the number of Ag nanoparticles on the external surface of AC, compared to that inside pores. Fourier transform infra-red and X-ray photoelectron spectroscopy results show that the oxygen plasma treatment leads to an increase in oxygen-containing-functional groups, such as C–O and C=O, from 21.9% to 30.8%. Microbiological investigations by plate assay and shake flask tests confirmed the antibacterial nature of the AC–Ag hybrid, showing an order of magnitude increase in death rate constant from 3.72 to 41.88 h⁻¹ on plasma treatment (rate constant means rate of loss of viable cell).

1. Introduction

Activated carbon (AC) is widely used as a filtration media in potable water production units for adsorption of organic contaminants [1]. It has a very high adsorption capacity due to its porous microstructure and the chemical nature of the carbon surface [2]. However, in addition, water intended for drinking should be free from fecal and total coliforms [3], which AC cannot ensure. Apart from use of AC, other promising water disinfection technologies are UV disinfection, and reverse osmosis (RO) membrane based water filtration system. UV exposure kills bacteria and virus to a certain extent, but it is not always effective, since either high levels of suspended solids, organic matter or colour reacts with UV radiation, resulting in decreased antibacterial properties [4]. On the other hand, RO membrane based system is a pressure driven process, in which a semi-permeable membrane rejects dissolved matter and microbes present in the water. However, bio-fouling may decrease membrane flux and shorten membrane life [5,6]. AC based water filter system is still most economical to remove taste, odor and other organic contaminants.

On the contrary, bacteria may actually prefer to adhere on the surface of AC, using the latter as the carbon source [7]. So, it is necessary to prevent bacterial growth on the AC surface. Hence, AC used for water purification should not only have good adsorption capacity, but also good antibacterial activity. In order to kill bacteria and other pathogens, silver (Ag) is used with AC as an antimicrobial agent [8]. Hence, it is a challenge to retain the primary nature of carbon surface for proper removal of contaminants and yet
ensure antibacterial property via good attachment of Ag to carbon.

One of the most important issues in antibacterial activity of Ag nanoparticles is release of Ag⁺ ions from particles, which is due to its oxidation in presence of water. Ag⁺ release can be controlled to a certain extent by using an appropriate Ag particle size, e.g., particles of 6 nm diameter have higher release (51%), in comparison to 25 nm diameter particles (5.8% release) [9]. A second important issue is aggregation of Ag nanoparticles in the dispersion due to attractive interparticle and surface forces. In order to prevent aggregation and thereby maintain effective antibacterial activity, surfactants and polymers have been widely investigated. However, actual implementations are limited due to the high cost and biocompatibility issues of these additives [10,11]. Other inorganic materials such as TiO₂, ZnO, and Cu have also been investigated to understand their antibacterial properties [12–14].

Recent reports in literature have discussed embedding Ag nanoparticles on various porous carbon platforms – including carbon nanotube, carbon aerogel, and AC – for inactivation of microbes as well as controlled release of Ag nanoparticles on various porous carbon and also inside the pores in these various carbon-forms. However, surface engineering of carbon for selective embedding of Ag nanoparticles only on the external surface of AC is required for efficient use of expensive, metallic Ag. The reason is as follows. Bacteria (like E. coli) are of dimension 1 μm or more, which would not be able to access Ag nanoparticles, whenever the latter are inside AC pores of size less than 1 μm. So, it is necessary to form Ag nanoparticles on the external surface of AC to facilitate inactivation of microbes in a more effective manner. As Ag nanoparticles have strong interaction with such functional groups – e.g., hydroxyl, carboxyl, carboxyl present on a carbon basal plane [17,18] – a large number of Ag nanoparticles can be embedded strongly on the external surface of AC.

Few attempts have been made in the literature to change the physical and chemical properties of AC for increasing the density of these functional groups. Carbon surface was modified by a wet chemical treatment (e.g., by nitric acid) [19] to introduce carboxyl and carbonyl groups for embedding particles. The disadvantage of this treatment is the resulting structural damage of aromatic planes in both bulk and near surface carbon by nitronium ions [20]. Nitronium ion attack will lead to reduction in adsorption sites for organic contaminants on the carbon surface. Heat treatment, on the other hand, may result in reduction of surface area as well as surface oxygen functional groups [21–23]. In contrast, plasma treatment is an effective method to improve the interfacial adhesion during activation and etching processes [24]. The primary advantage is that plasma treatment enables dry modification on the external surface of AC without altering bulk properties. It is possible to create an environment for oxidative, reactive and inactive reactions by changing the plasma gas.

In this work, we have demonstrated selective engineering of the AC surface by oxygen plasma treatment, so as to have Ag nanoparticles mostly on the external surface of AC. This strategy is expected to achieve improvement in the death-rate of pathogens (like E. coli) in water, not only to make it potable, but also would have significant implications in being able to alter the surface-chemistry of carbon by a simple, solvent-free, purely physical protocol. The latter would be of general interest to a carbon scientist, interested in surface functionalization of carbon for various other applications.

2. Experimental details

2.1. Materials and methods

To synthesize Ag nanoparticles, silver nitrate (AgNO₃) was used as the Ag precursor along with trisodium citrate (Na₃C₆H₅O₇). The latter acted both as a reducing agent and a capping agent. Milli-Q grade water (resistivity 18.2 MΩ cm at 25 °C) was used for Ag nanoparticle synthesis.

2.2. Synthesis of Ag nanoparticles in aqueous solution

Ag nanoparticles were prepared by photochemical reduction, as shown schematically in Fig. 1. All experiments were performed in a dark condition to avoid unwanted photochemical decomposition of AgNO₃. In a typical synthesis, 70 ml of 0.01 M AgNO₃ was prepared in a beaker and mixed with 7 ml of 0.1 M Na₃C₆H₅O₇ at room temperature. The beaker was positioned vertically under UV radiation (365 nm wavelength, 8 W power UV lamp) inside a closed UV chamber for 24 h. The nucleation and growth of Ag nanoparticles were favored by UV irradiation. Na₃C₆H₅O₇ has three carboxylic groups, out of which two would bind to Ag, leaving the third on the Ag nanoparticle surface free; the latter stabilizing Ag nanoparticles by electrostatic repulsion [25].

2.3. Surface modification of AC by oxygen plasma and impregnation with Ag nanoparticles

Dry AC granules with high density polyethylene (HDPE) binder (10% by weight) were received from Filtrex Technologies Pvt Limited, Bangalore and used directly for plasma treatment. The mesh size of AC granules was 100×325, which corresponds to a granule size range between 44 and 149 μm. The role of HDPE binder is to adhere the AC granules in the form of a cylindrical filter-candle, used as the standard carbon-block in water treatment devices. We first treated the as-received AC with oxygen plasma [Harrick plasma cleaner PDC-32 G, RF (radio frequency) – 13.6 MHz, power – 18 W, pressure – 0.1 torr, plasma treatment time – 10 min] to introduce polar functional groups on the AC surface. Afterwards, 5 g of plasma treated AC samples were crushed lightly and mixed with 80 ml of synthesized Ag nanoparticle dispersion for impregnation. This mixture was stirred for 12 h at 300 rpm. Finally, the impregnated AC–Ag granules were filtered and dried at room temperature.

2.4. Characterization

Morphologies of samples were observed in a scanning electron microscope (SEM) (Hitachi S3400N), field emission gun-scanning electron microscope (FEG-SEM) (JSM-7600F) and transmission electron microscope (TEM) (Philips...
3. Results and discussion

3.1. Structural analysis

In Fig. 2a and b, SEM images of untreated and plasma treated AC samples are shown, respectively, clearly indicating that both untreated and treated AC have various sizes and shapes of pores. AC thus has a high adsorption capacity due to the presence of both micro and mesopores [2]. Commercially, AC is prepared from natural resources such as coconut shell, wood, coal, lignite, etc. As a result, different pore sizes and shapes are generated during carbonization and activation processes while making AC, which are not altered further due to plasma treatment.

Fig. 2c shows the TEM image and size distribution of Ag nanoparticles synthesized by photochemical reduction. The mean particle size is 28 nm with a standard deviation of 5 nm. Finally, FEG-SEM image in Fig. 2d nicely illustrates how individual Ag nanoparticles are impregnated on the external surface of plasma treated AC, highlighting the importance of plasma treatment, in making possible the desirable impregnation of Ag to be more on the external surface of plasma treated AC, in comparison to untreated AC. The white bright spots in Fig. 2d corresponds to Ag nanoparticles.

Next, to understand the effect of chemical functionalization (due to plasma treatment), specific surface area and pore volume were calculated from nitrogen adsorption–desorption isotherms. It is observed from the isotherms (Fig. S1 in the Supplementary information) that there is a sharp increase in nitrogen adsorption for both samples at very low relative pressure. This indicates the presence of micropores in both samples. The hysteresis loops in the samples indicate existence of mesopores. Table 1 shows that specific surface area, total and micro-pore volumes, for both untreated and plasma treated AC samples are almost the same. Thus, clearly, functionalization does not affect structural properties of AC; it only increases the polar functional groups on the surface of AC.

The UV–Vis absorption spectrum of Ag nanoparticles is shown in Fig. 3a. There is a peak in the spectrum at 425 nm, corresponding to the plasmon absorbance of nearly spherically-shaped Ag nanoparticles [26].

3.2. Surface composition

The XRD pattern of AC–Ag in Fig. 3b shows major peaks with 2θ values of 34.5°, 44.5°, 64.8° and 77.6°, assigned to (111), (200), (220) and (311) lattice planes of FCC metallic Ag (JCPDF card No. 04-0783), respectively [27], confirming the presence of Ag.

Fig. 4a and b are related to contact angle measurements for untreated and plasma treated AC samples, respectively. A drop of Millipore water was placed on the AC surface using a micrometric syringe. The contact angle value for untreated AC was 130° in Fig. 4a. After oxygen plasma treatment, surface of AC became completely wettable to water, due to an increase in polar functional groups, showing only a thin, flat layer of water in Fig. 4b, without any visible drop of water. This happens because, during plasma treatment, there was an addition of oxygen to the carbon surface, since oxygen free radicals react with carbon atoms located on the peripheral surface of the graphitic platelets [24]. As a result, there are more polar functional groups attached on the plasma treated AC. In general, there is an effect of pore density and microscopical features of the surface on contact angle of water. However, both untreated and plasma treated samples have similar structural properties in terms of pore size, shape and density (as shown in Fig. 2a and b); so these features do not affect contact angle. The decrease in contact angle in plasma treated sample is due to surface hydrophilicity, resulting from chemical functionalization.

The FTIR spectra of untreated and plasma treated AC is shown in Fig. 4c. Selection of oxygen plasma treatment time is based on temporal evolution of FTIR spectra of plasma treated AC samples, in the wave number range of 1900–1300 cm⁻¹. To this end, same quantities of carbon granule (2 mg) and KBr powder (50 mg) were taken for all the samples to estimate the increase in amount of surface functional groups (–CO=O) during plasma treatment. It was found that there was no increase in the peak area of –CO=O moieties after 10 min of treatment (Table 2).
Table 1 – Structural properties of untreated and plasma treated activated carbon.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micro pore volume (cm³/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AC</td>
<td>415.2</td>
<td>0.19</td>
<td>0.16</td>
</tr>
<tr>
<td>Plasma treated AC</td>
<td>425.22</td>
<td>0.20</td>
<td>0.17</td>
</tr>
</tbody>
</table>
The spectra have four main peaks in the wave number range from 1800 to 1400 cm\(^{-1}\). The peak at 1700 cm\(^{-1}\) can be attributed to \(-\text{C=O}\) stretching vibrations of carboxyl group, whereas the peak at 1645 cm\(^{-1}\) corresponds to \(-\text{C=O}\) stretching vibration in quinones. The peak around 1550 cm\(^{-1}\) can be attributed to \(-\text{C=O}\) stretching vibration in ketones, whereas the peak at 1460 cm\(^{-1}\) is due to \(-\text{OH}\) deformation of carboxyl groups [28,29]. Thus, FTIR spectra reveal that there are more intense peaks of oxygen containing functional groups in the plasma treated sample. This indicates that there are more polar functional groups on AC surface after plasma treatment.

The surface composition of untreated and plasma treated AC can also be determined by XPS shown in Fig. 4d and e, respectively. The percentage of carbon and oxygen in these two samples were calculated from C1s and O1s spectra and given in Table 3. The untreated AC sample contains 78.0% carbon and 21.9% oxygen, while plasma treated AC contains 69.19% carbon and 30.8% oxygen. It reconfirms that there is an increase in oxygen content in the form of polar functional groups, which leads to more hydrophilicity. Table 4 shows the concentration of surface chemical groups present in the untreated and plasma treated AC, which was calculated using

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**Table 2 – Peak area of surface functional groups in untreated activated carbon and plasma treated activated carbon.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Plasma treatment time (min)</th>
<th>Peak area</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Carboxyl (C=O) ((1700 \text{ cm}^{-1}))</td>
</tr>
<tr>
<td>Untreated AC</td>
<td>0</td>
<td>108.40</td>
</tr>
<tr>
<td>Plasma treated AC</td>
<td>2</td>
<td>129.91</td>
</tr>
<tr>
<td>Plasma treated AC</td>
<td>4</td>
<td>140.28</td>
</tr>
<tr>
<td>Plasma treated AC</td>
<td>6</td>
<td>150.29</td>
</tr>
<tr>
<td>Plasma treated AC</td>
<td>8</td>
<td>174.55</td>
</tr>
<tr>
<td>Plasma treated AC</td>
<td>10</td>
<td>176.98</td>
</tr>
</tbody>
</table>

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**Fig. 4 – Contact angle measurement of (a) untreated AC and (b) plasma treated AC; (c) FTIR spectra of untreated and plasma treated AC; XPS spectra of (d) of untreated AC and (e) plasma treated AC.**
C1s spectra. The observed C1s spectra have a binding energy range from 281.0 to 291.0 eV, which are attributed to carbon based functional groups.

The C1 s spectra were deconvoluted into four peaks by using XPS peak 41 software. The peak at 284.6 eV corresponds to graphitic carbon (C–C) bond, while peak at 285.8 eV corresponds to hydroxyl (C–OH) or ether (C–O–C). The peak at 287.4 eV corresponds to carbonyl group in ketones and quinines (C=O), while peak at 288.5 eV corresponds to carboxyl (COOH) group [29,30]. The untreated AC contains 73.8% C–C, 17.4% C–OH or C–O–C and 5.4% C=O groups, whereas the plasma treated sample contains 69.9% C–C, 21.52% C–OH or C–O–C and 11.67% C=O groups. It is clear that on plasma treatment, polar functional groups such as hydroxyl, carbonyl and carboxyl groups increased, while graphitic carbon group decreased.

3.3. Elemental analysis

Table 5 shows the amount of Ag in the untreated AC and plasma treated AC determined by ICP-AES and EDX. The results prove the presence of Ag nanoparticles in the hybrid.

Table 3 – Composition (atomic wt.%) by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C</th>
<th>O</th>
<th>O/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AC (%)</td>
<td>78.1</td>
<td>21.9</td>
<td>0.28</td>
</tr>
<tr>
<td>Plasma treated AC (%)</td>
<td>69.2</td>
<td>30.8</td>
<td>0.45</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>C–C (284.6 eV)</th>
<th>C–OH, C–O–C (285.8 eV)</th>
<th>C=O (287.4 eV)</th>
<th>COOH (288.5 eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated AC (%)</td>
<td>73.8</td>
<td>17.4</td>
<td>5.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Plasma treated AC (%)</td>
<td>60.9</td>
<td>21.52</td>
<td>11.67</td>
<td>5.91</td>
</tr>
</tbody>
</table>

During plasma treatment, oxygen free radicals react with carbon atoms located on the peripheral surface of the graphitic platelets of AC. This surface treatment creates more oxygen-containing polar functional groups (–COOH, –C=O, etc.) to be attached on the plasma treated AC. As these oxygen-containing functional groups form coordinate bonds with Ag nanoparticles, external surface of plasma treated AC will have more Ag nanoparticles in comparison to untreated AC surface. Even though the amount of total Ag loading is almost the same in both untreated and plasma treated AC samples (measured to be 0.9 wt.% approximately, by ICP-AES), plasma treatment contributes in increasing more Ag loading on the external surface of AC, proved by elemental mapping in Fig. 5(e–h).

3.4. Antibacterial activity

In the plate assay test, melted M-Endo agar (Himedia) was prepared and then 1 ml diluted E. coli (grown overnight)
culture was added to it so as to have $10^3$ colony forming units per ml agar.

About 20 ml of seeded agar was added to sterilized petri plates and then solidified by refrigerating for 4–6 h. A circular hole (7 mm diameter) was made in the seeded agar using a sterilized borer. About 30 mg of AC–Ag was added in the well with 2 drops of sterilized water. The plates were incubated at 37 °C for 20 h and the inhibition zone was measured. The untreated and plasma treated AC with Ag sample gave an inhibition zone of 5 mm diameter (Fig. 6a).

Shake and plate assay tests were done to assess the antibacterial activity of Ag impregnated AC granules, using
E. coli. In shake flask test, 50 ml of saline water was taken and inoculated with E. coli, so as to have 4200 cells in the shake flask. Then, 0.5 g of AC–Ag was added to it and contents were stirred in a rotary shaker at ambient temperature. Samples were drawn periodically from the flask and tested for number of surviving E. coli by the plate count method. Shake flask test was done for untreated AC with Ag as well as plasma treated AC with Ag (Fig. 6b). The latter has shown better antibacterial effect in comparison to untreated AC–Ag with Ag. Plasma treated sample with Ag took 10 min to kill all the bacteria, whereas untreated sample took 1 h. The reason being an increase in polar functional groups on the surface of AC due to oxygen plasma treatment. This results in a much better chance of Ag nanoparticles on the external surface, leading to better accessibility of E. coli and direct contact in the plasma treated sample, compared to untreated AC–Ag, where Ag particles would be distributed both inside the pores of AC and on the external surface. Plasma treated AC–Ag has an order of magnitude higher death rate constant (41.88 h⁻¹) in comparison to untreated AC–Ag (3.72 h⁻¹) (Fig. 6c).

Table 6 shows comparison of present work versus recent reports in the literature in terms of percentage of Ag in the hybrid and the resulting antibacterial activity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Bacteria</th>
<th>Ag (wt%)</th>
<th>Rate constant (h⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag nanoparticles embedded on the external surface of activated carbon fiber</td>
<td>S. aureus</td>
<td>0.92</td>
<td>0.538</td>
<td>[7]</td>
</tr>
<tr>
<td>Ag nanoparticles embedded on the external surface of activated carbon fiber</td>
<td>K. pneumoniae</td>
<td>0.92</td>
<td>0.530</td>
<td>[7]</td>
</tr>
<tr>
<td>Ag nanoparticles embedded inside and external of activated carbon aerogel</td>
<td>E. coli</td>
<td>1.4</td>
<td>1.53</td>
<td>[15]</td>
</tr>
<tr>
<td>Ag nanoparticles embedded inside and external surface of activated carbon</td>
<td>E. coli</td>
<td>11.36</td>
<td>32.00</td>
<td>[1]</td>
</tr>
<tr>
<td>Ag nanoparticles are selectively embedded more on the external surface of activated carbon</td>
<td>E. coli</td>
<td>0.89</td>
<td>41.88</td>
<td>Present work</td>
</tr>
</tbody>
</table>

Table 6 – Comparison of antibacterial effect of AC–Ag.
4. Conclusions

The present work explains the role of polar functional groups in embedding more Ag nanoparticles on the external surface of AC and its antibacterial activity. Ag nanoparticles were impregnated in both untreated AC and oxygen plasma treated AC. The percentage of Ag nanoparticles impregnated in both kinds of samples were almost same, about 1 wt.%. However, plasma treated AC with Ag nanoparticles show much higher death rate constant for E. coli (41.88 h⁻¹) in the shake flask test, compared to untreated AC with Ag nanoparticles (3.72 h⁻¹). This is because after plasma treatment, external surface of AC turned hydrophilic due to an increase in carboxyl and hydroxyl groups on the external surface of plasma treated samples, by way of reaction between carbon of AC and oxygen in the plasma. This leads to impregnation of Ag nanoparticles on the more accessible external surface of AC, rather than the interiors of the AC pore; since micrometer-sized E. coli may not penetrate inside the smaller pores of AC during flow of water through the AC–Ag hybrid. Plasma treated AC with Ag nanoparticles hybrid has thus shown a great potential in the area of water disinfection, ensuring a much faster death rate of harmful pathogens in potable water.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbon.2013.01.008.

REFERENCES


