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Bactericidal Efficacy of Silver Impregnated Activated Carbon for Disinfection of Water

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Abstract. When highly contaminated water was passed through two types of silver coated activated carbon and their mixtures with sand, the former was found to be far better medium for disinfection of water, with bactericidal efficacy of about 2.5 times that of the latter.

Keywords: bactericidal efficacy, activated carbon, water disinfection, silver impregnation

Introduction

For provision of safe drinking water, the bacteriological quality of water is of paramount importance in addition to monitoring of indicator bacteria such as coliform and faecal coliforms, effective gadgetries and means and devices for providing safe drinking water, as per WHO standards (WHO, 1984).

The germicidal effect of silver was first explored by Carlon in 1893; since then several devices containing silver as water disinfectant have been proposed and their bactericidal efficacy has been investigated (Kim *et al.,* 2008; Bell, 1991; Pierce *et al.,* 1978; Berger *et al.,* 1976; Barranco *et al.,* 1974; Spadaro *et al.,* 1974). In addition to being bactericidal, silver also increases the lability of viruses when used for disinfection of water (Mahnel and Schmidt, 1986). Some bacteria can develop resistance to silver (Russell *et al.,* 1994) but other evidence suggests that no resistant strains have been encountered clinically (Lansdown, 2002). Activated carbon/coal-based sorbents have been observed to remove enteric viruses satisfactorily (Chaudhri and Sattar, 1989; 1986). Activated carbon is unique and versatile adsorbent because of its extensive surface area, microporous structure and high adsorption capacity; hence, it is widely used as filter medium in drinking water purification devices (Jayadev and Chaudhri, 1990; Osman and Chaudhuri, 1990; Prasad and Chaudhuri, 1989; Protheroe *et al.,* 1989; Tikhonova *et al.,* 1989). Activated carbon is also assuming increasing importance in the control of air pollution, in purifying and controlling the general chemical environment, in certain biomedical applications and for removal of organic matter from water and wastewater (Usmani *et al.,* 1994).

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In the present work, samples of granular activated carbon, prepared locally from an indigenous raw material, and imported granular carbon were coated with silver and used for disinfecting water. The objective of the study is to assess and compare the disinfection efficacy and capability of the two types of silver coated products, separately as well as mixed with untreated graded sand.

Materials and Methods

The imported activated carbon used in this study was granular carbon of M/s. Norit, Holland. The locally produced granular activated carbon was prepared from coconut shells. The shells were first disintegrated in a pilot disintegrator followed by carbonization in an inert atmosphere of nitrogen void of air and then physically activated with a mixture of superheated steam and air in a fluidized bed reactor (Usmani *et al.,* 1999). Both activated carbon samples i.e. imported (I) and locally produced (L), were broken in a rod mill, classified to a particle size of 1.00-2.00 mm on a sieve shaker and then utilized for impregnation of silver. The samples were initially washed thoroughly with water to get rid of any foreign material etc., and then dried at 120 °C to constant weight, prior to silver coating.

Silver was impregnated on both carbon samples by the method described by Beg *et al.* (1986) for the treatment of sand. Briefly, 500 g of graded, washed and dried sample of each activated carbon was treated with 0.1% A.R. grade silver nitrate solution, allowed a maturing time of one h and then treated with 10% sodium hydroxide solution. Carbons samples were then initially treated with 10 ml 1:1 NH_4OH solution and afterwards with 15 ml of reducing sugar solution washed with distilled water to pH 7 and then finally dried at 120 °C.

The respective activated carbon sample (1000 g), either alone or a mixture with sieved, graded, washed and dried sand in the ratio of 1:1, was placed into a cylindrical plastic container 4″x 12″. The cycling have adjustable inlet and outlet PVC valves at the top and bottom, respectively, and a polyethylene screen of suitable mesh size at the bottom for supporting the carbon or carbon-sand mixture in the container. In column ‘1’, in which there was only silver coated carbon, the mass of carbon was 1.34 kg and that of silver was 2.68 g. In column ‘2’, in which there was mixed bed of 1:1 silver coated carbon and untreated sand, the masses of carbon, sand and silver were 1kg, 1kg and 2 g, respectively. Mass transfer limits have influenced the results as may be seen in Table 5-6. The whole study was performed at a flow rate of one litre/min of water passing through the columns and empty bed, whereas, contact time in both the cases was five minutes.

Experiments were carried out, using artificially contaminated feed water having chemical and microbiological analysis as shown in Table 1, to asses the disinfection efficiency of silver impregnated activated carbon samples and carbon-sand mixtures. The water was artificially contaminated with common indicator organisms *E. coli* in the range of 10^3-10^4/100 ml. A sample was drawn from the bulk of well mixed contaminated feed water and termed as “Control”. The contaminated water was passed through plastic containers packed with silver coated locally produced and imported activated carbon samples and also through mixtures of graded sand and silver coated activated carbon and graded sand at a flow rate of 1 litre/min. Samples of water after passing through the plastic containers were collected in sterile flasks and alongwith the control, subjected to microbiological and, silver analyses to compare the disinfection efficacy of the activated carbons alone and carbon-sand mixtures and also to determine the amount of released silver in treated water.

Microbiological tests were performed according to the methods described in American Public Health Association Standard Methods (APHA, 1998) and WHO standards (WHO, 1984). For presumptive coli tests two sets, each consisting of three tubes containing 10 ml, 1 ml and 0.1 ml of the sample in MacConkey broth, were used; one set was incubated at 37 °C for 24 h and the other at 44 °C for 48 h. Most Probable Numbers (MPN/dl) were ascertained from McGrady’s table.

Analysis of eluted silver in treated water samples was performed on Z-8000 Hitachi atomic absorption spectrophotometer with Zeeman effect background corrections equipped with a graphite furnace, a microprocessor and a built-in printer. Determination of silver was carried out by flameless (ETAAS) atomic absorption spectrometry employing standard addition technique (APHA, 1998).

Results and Discussion

In an earlier study of the bactericidal efficacy of silver coated sand mixtures, Mahmood *et al.* (1993) obtained upto 1800 litre, microbiologically safe water (coliforms and faecal coliforms <3 MPN/dl), however, the efficacy of silver coated sand mixture dropped significantly, after passage of 2000 litre of contaminated feed water. The present study has been carried out to assess the efficacy of silver coated granular carbon samples (L and I), either alone or as mixture with untreated, washed and graded sand.

All the chemical parameters of feed water used in the present study were within permissible limits (Table 1). Locally produced granular activated carbon sample (L), prepared by fluidized bed activation of coconut shells, had better physical and chemical characteristics as compared with the imported sample (I) of NORIT, Holland (Table 2).

The data recorded in Table 3-4 relate to disinfection of contaminated feed water, after passing through the containers packed with silver coated activated carbon and their 1:1 sand mixtures. The holding time of contaminated water in both the cases was almost zero and samples were drawn immediately after feeding of contaminated water. It was observed that feed water was highly contaminated having coliform and faecal coliform 1100^+ MPN/dl, before treatment with silver coated activated carbon, whereas, the number of coliforms on the water, after treatment with both the carbon samples, reduced

Table 1. Chemical and microbiological analysis of feed water

Parameters	Measured value ± SD
Chemical analysis	
pH	7.1 ± 0.1
Electrical conductivity	588 µg/cm ± 8
Calcium	35 mg/l ± 0.8
Magnesium	11 mg/l ± 0.8
Sodium	37 mg/l ± 0.5
Potassium	06 mg/l ± 0.2
Chloride	49 mg/l ± 1
Sulfate	54 mg/l ± 4
Bicarbonate	130 mg/l ± 4
Alkalinity	107 mg/l ± 3
Calcium hardness	87 mg/l ± 1
Magnesium hardness	45 mg/l ± 1
Total dissolved solids	338 mg/l ± 5
Microbiological tests	
Coliforms (MPN/dl)	>1100
Faecal coliforms (MPN/dl)	>1100

significantly to <3, which is of desired WHO standard (WHO, 1984). The data further reveals, that safe water, as per WHO standard, was obtained for the first 4400 litre of feed water in both the samples ‘L’ and ‘I’. Afterwards, in both the cases, this number gradually increased. However, treated water samples obtained after passing 4600 and 4800 litre of contaminated water through carbon sample ‘L’ had comparatively less coliforms (9 and 23 MPN/dl, respectively) than that of carbon sample “I” (23 and 43 MPN/dl) (Table-3). This comparatively better bactericidal efficacy of the local carbon sample (L) may be due to its better adsorptive properties, higher surface area and lower bulk density (Table 2).

A critical review of the data obtained in case of 1:1 carbon-sand mixtures (‘LS’ and ‘IS’) (Table 4), clearly indicates that bactericidal efficacy of both silver coated carbon samples is drastically affected and disinfection capacity is reduced upto almost 50% (2200 litre), when they were mixed with sand in equal proportions (‘LS’ and ‘IS’).

Several studies have been reported in literature indicating that silver impregnated activated carbon filters used in disinfection of water are suspectible to colonization and after some time shed bacteria into the water (Taylor *et al.,* 1979; Burkhead *et al.,* 1978; Hanes, 1978; Wallis *et al.,* 1974; Fiore and Babineau, 1971). However, contrary to the observations of Pierce *et al.* (1978), the present results (Table 3), clearly suggest that silver coated carbon effectively and significantly disinfect contaminated water and that activated carbon is a promising and potential medium for impregnation of silver for disinfection of water. Further, its disinfection efficacy up to 4400 litre of highly contaminated water, is far better than the other silver coated media like sand (Mahmood *et al.,* 1993). Disagreement between the results obtained in this study with those of other workers, with reference to bactericidal efficiency of the two silver coated carbon samples, may be due to the difference in the method of treatment adopted for coating of silver on activated carbon samples. This method may have resulted in a more effective and long lasting impregnation of silver on carbon which is thus released gradually in contaminated water in just sufficient quantity required for its oligodynamic bactericidal action for disinfection of water. This point has further been substantiated by the systematic study carried out on the quantitative estimation of the amount of silver eluted with the passage of a certain amount of water *viz* 50, 100, 200, 400, 600 litre, through silver impregnated activated carbon samples at a flow rate of 1 liter/min, established after a series of experiments. Level of silver up to 0.7 mg/litre (0.1 ppm) can be tolerated without any risk to health (WHO, 2003).The results (Table 5), clearly show that the amount of silver being released is gradual and regular and that the silver coated carbon samples ‘L’ and ‘I’ are effective for the disinfection of highly contaminated water in the silver elution range of 11-56 ppb.

Table 2. Main physical and chemical characteristics of granular activated carbon samples

Characteristics determined	Locally produced sample (‘L’) (Measured value ±SD)	Imported sample (‘I’) (Measured value ±SD)
Bulk density	0.5028 g/cc ± 0.005	0.5892 g/cc ± 0.006
Ash content	1.35% ± 0.01	2.03% ± 0.02
Iodine	1036 mg/g ± 10.4	818 mg/g ± 8.2
Methylene blue	247 mg/g ± 4.8	190 mg/g ± 3.8
Carbon tetra		
Chloride adsorption	60% ± 3	54% ± 2
BET surface area	950 m^2/g ± 9.20	810 m^2/g ± 7.9

Table 3. Disinfection of contaminated feed water after passing through silver coated activated carbon samples

Water passed (litre)	L(MPN/dl)	I(MPN/dl)	Control
50-4400	<3	<3	1100^+
4600	9	23	1100^+
4800	23	43	1100^+

Table 4. Disinfection of contaminated feed water after passing through 1:1 mixture of graded sand with locally produced (LS) and imported (IS) activated carbon samples

Water passed (litre)	LS(MPN/dl)	IS(MPN/dl)	Control
50-2200	<3	<3	1100^+
2400	4	4	1100^+
2600	21	21	1100^+
2800	43	43	1100^+
3000	43	43	1100^+
3200	93	93	1100^+
3400	150	150	1100^+
3600	1100^+	1100^+	1100^+
3800	1100^+	1100^+	1100^+
4000	1100^+	1100^+	1100^+
4200	1100^+	1100^+	1100^+
4400	1100^+	1100^+	1100^+
4600	1100^+	1100^+	1100^+
4800	1100^+	1100^+	1100^+

It may be further noted that the amount of silver, released from the coated activated carbons gradually and steadily decreases with the increasing volume of contaminated water passing through carbon. Moreover, there is a definite correlation (Table 5 and 6) between the amount of silver released (ppb) by the silver coated carbon samples in the treated water and their bactericidal efficiency (Masaru, 1991; Yoshinari, 1989). In either of the cases, safe water of MPN/dl<3 was obtained upto minimum silver elution limit of 11 ppb. Afterwards, when the release silver is less than 11 ppb, the bactericidal property of silver is markedly inhibited, as may be seen by the higher MPN/dl of 23 and 43 obtained in product water samples of 'L' and 'I', respectively, which is definitely higher than the desired WHO standard. A somewhat identical pattern of the systematic and gradual release of oligodynamic element, although in smaller quantity, logically due to comparatively lesser amount of impregnated silver available in the mixture of carbon and sand samples 'LS' and 'IS' than carbon samples 'L' and 'I', was found (Table 6). This data further confirms the threshold limit of 11 ppb silver, just the minimum quantity required for bactericidal action/disinfection of water. Data (Table 5 and 6) further confirms that silver impregnated carbon is a better medium for providing safe drinking water, as its silver elution is within permissible limits. 'Safe Drinking Water Act' in USA. requires that siwer content in drinking water should be below 50 ppb (Oya *et al.,* 1994). In the present study, the amount of silver ions eluted in samples 'L' and 'I' is slightly >50 ppb in the first 50 litres of water (Table 5); however this excess silver may be initially removed by washing with water while using coated activated carbon for obtaining disinfected potable water.

Table 5. Estimation of the amount of silver in treated water after passing through silver coated activated carbon samples

Water passed (litre)	Silver concentration in Water(ppb) (L)	Silver concentration in Water(ppb) (I)
50	56	56
100	49	48
200	48.1	46.1
400	46.2	42.4
600	38.3	39.8
800	34.2	32.2
1000	33.6	30.7
1200	32.1	28.8
1400	29.9	26.2
1600	28.7	25.4
1800	26.4	24.0
2000	25.1	22.7
2200	23.9	21.9
2400	22.7	21.1
2600	21.4	20.5
2800	20.1	19.3
3000	19.0	18.1
3200	18.8	17.5
3400	17.7	16.8
3600	16.5	15.7
3800	15.8	14.6
4000	14.9	13.8
4200	13.0	12.9
4400	11.2	11.0
4600	10.1	10.2
4800	9.2	9.4

Table 6. Estimation of the amount of silver in treated water after passing through silver coated carbons and mixtures

Water passed (litre)	Silver concentration in Water(ppb) (LS)	Silver concentration in Water(ppb) (IS)
50	26.7	26.1
100	25.2	25.0
200	24.1	24.2
400	23.2	22.8
600	21.1	20.9
800	21.5	19.5
1000	19.2	18.0
1200	18.0	16.9
1400	17.0	15.4
1600	16.1	14.2
1800	14.9	13.1
2000	12.2	12.0
2200	11.3	11.3
2400	10.1	10.1
2600	9.4	8.7
2800	8.2	7.6
3000	7.1	6.2
3200	6.2	5.4
3400	5.0	4.8
3600	4.3	3.7
3800	3.2	2.3
4000	2.3	1.2
4200	1.0	0.29
4400	0.18	-
4600	-	-
4800	-	-

Conclusion

It may be inferred from the study that though activated carbon is comparatively more expensive than the graded sand, but it is a better medium than graded sand for impregnation of silver to be used for water disinfection /decontamination. The bactericidal efficacy of silver coated activated carbon, obtained by the specific coating technique developed by Beg *et al.,* (1986) is about 2.5 times higher (4400 litre) than that of coated graded sand mixture (1800 litre), for disinfection of highly contaminated water. The technology for the preparation of granular activated carbon from an indigenous raw material, used for coating of silver is locally available. However, this is a preliminary study; further investigations to assess the effects of various variables such as exposure time, pH, temperature, chemical quality of water etc., are required so that this effective and inexpensive technology may be used for water sanitization.

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