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Removal of superparamagnetic corrosion products and contaminants from drinking water using activated carbon

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ABSTRACT

Particulate matter separated from tap water using columns of coarse and fine activated carbon was characterized by means of chemical analysis, magnetization measurements, X-ray diffraction (XRD) and scanning electron microscopy (SEM)—energy dispersive X-ray spectrometry (EDS). A large fraction of the solids accumulated on the activated carbon consisted of iron oxides, in particular magnetite nanoparticles, and of iron oxyhydroxides, specifically goethite and lepidocrocite. These species formed as a result of corrosion of iron or carbon steel pipes. The removal of various iron species was measured using a two-column system consisting of a column of coarse activated carbon followed by a column of fine activated carbon. The results indicated that coarse activated carbon was only effective in removing oxyhydroxide particles, while the fine activated carbon was also able to remove nanoparticles of anhydrous iron oxides such as magnetite and maghemite. In addition, it was observed that while a majority of the content of contaminants, such as lead and copper, was removed upon passing the water through the coarse activated carbon, a significant fraction of the contaminant content was only removed upon subsequently passing the water through the fine activated carbon. It was concluded that most of the content of lead, copper, and other contaminants was associated with the iron oxyhydroxides, but a sizeable fraction was associated with the magnetite nanoparticles. Thus, the results supported the assumption that the presence of contaminants associated with magnetite nanoparticles in drinking water can be a significant mode of contaminant transport through water distribution systems.

Keywords: Nanoparticles; Activated carbon; Iron; Contaminants; Drinking water

1. Introduction

Modern water purification plants are highly effective in removing contaminants from natural water in order to meet the demanding standards required for drinking water. However, before the treated water reaches the consumer, it passes through a pipe system in which the water may become re-contaminated with hazardous species such as lead and copper.

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Commercial household filters are used to remove such hazardous species prior to use by the consumer. Such filters, often consisting of mixtures of ion-exchange resins and activated carbon with a fairly large grain size, are quite effective both in filtering out coarse particles and in removing dissolved metal ions through ion exchange. However, it is much more difficult to remove nanoparticles than it is to remove coarse particles or dissolved ions. The nanoparticles that are most likely to be present in municipal water systems consist of corrosion products such as iron oxides (e.g., magnetite and maghemite) and oxyhydroxides (most commonly, lepidocrocite, and goethite) which result from the corrosion of pipes and valves. The speciation of corrosion products of iron and steel has been investigated in detail and reviewed in several books and book chapters [1–4]. Oxides and oxyhydroxides formed as a result of corrosion of mild steel have been shown to contain particles in the 10 nm size range of goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH) and magnetite [5]. Oxide and hydroxide nanoparticles are formed as a result of corrosion of carbon steel pipes and valves [6] as well as corrosion of other metallic materials. Phenomena that aggravate materials degradation, such as erosion-corrosion, can result in the formation of colloidal nanoparticles even from durable alloys such as stainless steel [7]. Consequently, nanoparticles can be detected in drinking water passing through the pipes of distribution systems [8].

Pure nanoparticles of iron oxides and hydroxides in water can be expected to be harmless to human health. However, such iron compounds may adsorb contaminants and transport them to the point of use of the water by the consumer. Iron oxyhydroxides, such as goethite and lepidocrocite, are well known to have high adsorption capacities regardless of particle size [9]. On the other hand, the adsorption capacities of coarse particles of anhydrous iron oxides, such as magnetite, are very low. However, as the size of magnetite particles decreases, their adsorption capacities increase [10–12], and magnetite nanoparticles are effective adsorbents for contaminants such as Cr [13,14], Cu [14], U [15], and As [10–12]. The reason for the higher activity of the nanoparticles, as compared with coarse particles, is that the specific surface area of the nanoparticles is much larger, and a much larger fraction of the magnetite is present at the surface, where the bond structure is incomplete, resulting in higher energy states with much higher reactivity toward adsorbable species.

When commercial household filters containing activated carbon are flushed before use, it is generally recognized that most of the fine carbon particles are removed from the filters. However, some of the fine carbon particles are found to remain in the filters. Magnetic measurements previously conducted on filters which had been used for 2–3 months to clean tap water [16] showed that superparamagnetic magnetite was captured by fine carbon particles trapped inside these filters. Superparamagnetic magnetite consists of particles that are smaller than domain size (about 50–100 nm). In such small particles, some of the magnetic ions become randomized due to thermal motion and their alignment begins to break down. As a result, as particle size decreases below the domain size, the material no longer exhibits strong, permanent, field-independent magnetization, and the magnetization becomes more and more dependent on the external magnetic field, that is, the magnetic behavior gradually assumes a paramagnetic, rather than a ferromagnetic, character. It should be noted that the presence of superparamagnetic corrosion products with a size of the order of 10 nm was observed in studies of corrosion scale formed on mild steel [5].

We have further observed that when tap water containing nanoparticles of magnetite is allowed to flow through a commercial carbon filter after preflushing, most of the nanoparticles of magnetite are not removed from the water. Why is it that the residual fine carbon particles do not remove all of the magnetite from the flowing water? There are two or more possibilities: (1) the amount of magnetite in the water may be much larger than the available "parking spaces" on the remaining fine particles of activated carbon, or (2) the contact time of magnetite with the residual fine carbon is too short for the absorption process to take place. These two or other possibilities may account for the passage of magnetite through the washed filter.

In addition to the above carbon filters, we have also observed [17] that contaminants such as lead (Pb), copper (Cu), and arsenic (As) are present in magnetite nanoparticles sorbed on membrane filters. This may be expected, as small, high specific area, subdomain particles of magnetite have a large sorption capacity for contaminants [18].

In this study, we used columns of coarse and fine activated carbon to remove the magnetite nanoparticles and the contaminants sorbed on them. Clustering of magnetite was sometimes used to account for the removal of nanoparticles upon passage through membrane filters in which the pore sizes are much larger than those of the nanoparticles [17]. The performances of columns of coarse and fine activated carbon, respectively, in removing nanoparticles from tap water were evaluated in this study.

2. Materials and methods

2.1. Water samples

Samples were obtained from cold water taps in a 90-year-old building in Washington, DC. The water main that delivers water to the building is an underground cast iron pipe, while most of the water supply lines inside the building are made of copper with soldered joints.

2.2. Experiments with columns of activated carbon

Two sizes of steam-activated carbon derived from coconut shells were used for the experiments. The coarse carbon was Fisher Scientific 05-685A, –6 + 14 mesh (3.35–1.4 mm). The fine carbon was Fisher Scientific 05-690A, –50 + 200 mesh (300–75 μm). The inorganic impurities in each grade of activated carbon were determined by extracting the inorganic species with a hot HCl solution. The extract was diluted with de-ionized water and analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES). The spectrometer used for the analysis was Perkin-Elmer Plasma 400. In addition to the activated carbon used for the analysis of impurities, a quantity of 16 g of each type of activated carbon was weighed out and then subjected to magnetic sweeping [16] with a strong neodymium-based magnet (Edmund Scientific 3081237). The magnetic sweeping was repeated under 2-propanol. The few carbon particles that showed magnetic activity were removed, and the 2-propanol was discarded. Using de-ionized water, the carbon was then washed and loaded into glass columns.

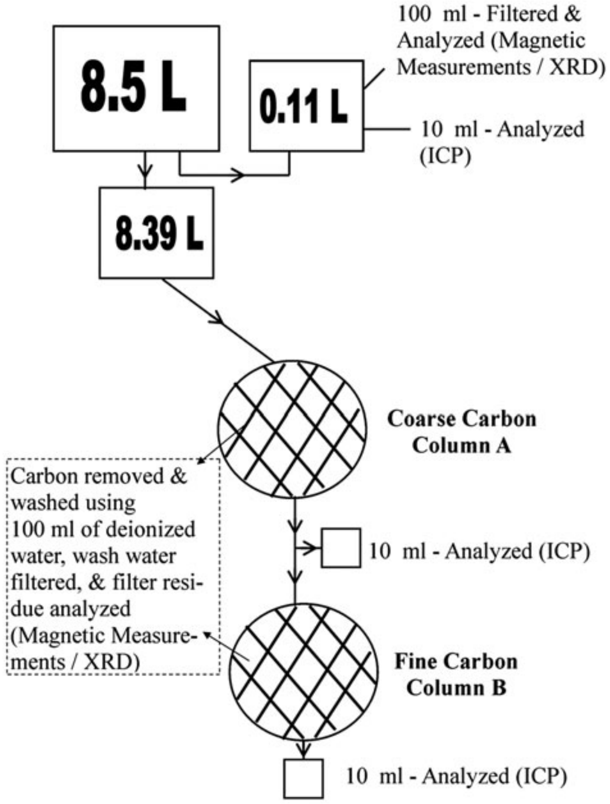

Fig. 1. Flow diagram showing the experimental procedures used for the analysis of water samples.

The procedure used in the adsorption experiments is illustrated in the schematic flow diagram of Fig. 1. As shown in Fig. 1, in each experiment an original volume of 8.50 L of tap water was homogenized by shaking, and a 10 mL sample was removed and acidified with 0.5 mL of concentrated HCl to dissolve the suspended solids. The sample was then analyzed using ICP-AES. In addition, a 100 mL aliquot of the 8.50 L sample was filtered through a 0.22-μm membrane filter to separate the suspended solids from solution. It had been shown previously that a 0.22-μm membrane filter removes all particulates from the water [17]. The solids accumulated on the membrane filter were characterized by means of X-ray diffractometry (XRD) and magnetization measurements [16]: A JEOL scanning electron microscope (SEM) with a Bruker energy dispersive spectrometer (EDS) was also used. The remaining water (8.39 L) was passed through a bed of coarse activated carbon, 2 cm in diameter and 14 cm high, designated Column A, at a flow rate of approximately 0.5 mL/s. When 99.9% of the water had passed through Column A, the flow was terminated. During the passage of water through Column A, solids were accumulated on the coarse carbon bed. The activated carbon from Column A was subsequently removed and washed using 100 mL of de-ionized water. The wash water was filtered through a 0.22-μm membrane filter, and then the filter was dried, and the residue remaining on the filter was characterized using magnetization measurements and XRD, as described for the original water above. The entire volume of the effluent from Column A was homogenized by shaking, and then a 10 mL sample of the effluent was removed, acidified with HCl, and analyzed using ICP-AES. The rest of the effluent of Column A (approximately 8.29 L) was passed through a similar column packed with fine activated carbon, designated Column B. Once again, when 99.9% of the Column A effluent had passed through Column B, the flow was terminated. During the passage of water through Column B, solids were accumulated on the fine carbon bed. The activated carbon from Column B was subsequently removed and washed using 100 mL of de-ionized water. The wash water was filtered through a 0.22-μm membrane filter, and then the filter was dried, and the residue remaining on the filter was characterized using magnetization measurements and XRD. The effluent from Column B was homogenized by shaking, and then a 10 mL sample of the effluent was removed, acidified with HCl and analyzed using ICP-AES.

3. Results

The results of the initial analysis performed on two grades of activated carbon before the start of the experiments are shown in Table 1. Upon magnetic sweeping, the number of activated carbon grains exhibiting magnetic activity was found to be very small in both the coarse carbon and the fine carbon.

The tap water used in the column experiments contained a light brown suspension of solid particles, and its pH was 7.50. Following solubilization with acid, analysis of the three samples (original water, Column A effluent, and Column B effluent) produced the results shown in Table 2. The results of XRD measurements on the solids separated from each of the three samples by means of filtration through 0.22-μm filters are shown in Table 3 and Fig. 2. Although the signal-to-noise ratio of the diffractograms was limited by the small amounts of solids that could be obtained from the tap water, characteristic peaks for the main corrosion products could be identified. The results in Table 3 show that most of the iron in the original tap water was present in the forms of lepidocrocite and goethite while a minor amount of iron was in the form of magnetite. The results further show that the lepidocrocite and goethite in the original water were picked up on the coarse carbon column (Column A), while the magnetite passed through it and was picked up on the fine carbon column (Column B). Magnetization measurements were performed on solids recovered from the original water, from the spent Column A, and from the spent Column B. The results show that the iron species accumulated on Column A were paramagnetic, in agreement with the predominance of α-FeOOH and γ-FeOOH in the XRD diffractograms. The results of the magnetization measurements on solids from column B at room temperature and at liquid nitrogen temperature are shown in Fig. 3(a) and (b), respectively. In contrast with the solids recovered from column A, the solids accumulated on Column B, after most of the iron compounds were removed by Column A (see Table 2), were observed to consist mostly of superparamagnetic Fe_3O_4 nanoparticles which had been previously shown to exist in tap water [16]. These Fe_3O_4 nanoparticles were, therefore, less efficiently trapped by the coarse carbon than the hydrated iron oxides. The presence of a strong superparamagnetic component showed that a large fraction of the magnetic species lay within the nanoparticle size range. Using the methodology described in Ref. [16], the particle size corresponding to the data shown in Fig. 3 was calculated to be $\geqslant 4.5\,\text{nm}$. The magnetic saturation data agree with the chemical analysis shown in Table 2 if most of the iron accumulated on

Table 1
Inorganic impurities in coarse and fine activated carbon, Fisher Scientific 05-685A and 05-690A

Element	Content, ppm	
	Coarse carbon, 05-685A	Fine carbon, 05-690A
K	7,471	7,007
Na	564	921
Si	438	1,516
Mg	405	411
Ca	359	824
Al	29	774
Fe	<10	417
Mn	7	23
Ni	7	16
Cu	5	16
Zn	4	5
Pb	2	6
Ti	1	68
As	1	15
Cr	1	3

Table 2
Elemental concentrations observed by ICP-AES in tap water before and after passing through columns of activated carbon

Element	Concentration, mg/L		
	Original water	Column A effluent	Column B effluent
Ca	44.7	46.3	50.6
Na	16.1	13.7	15.4
Mg	10.1	8.59	9.37
Fe	5.76	0.74	0.001
Zn	3.29	1.10	0.36
Cu	2.91	0.55	0.002
K	1.99	1.99	2.26
Si	1.30	1.54	1.72
Pb	0.91	0.17	<0.01
Al	0.53	0.23	0.20
Ba	0.13	0.055	0.053
Ni	0.11	0.069	0.048
Mn	0.11	0.11	0.11
Ti	0.012	<0.001	<0.001
Cr	0.011	0.022	0.012

Table 3
XRD characterization signals of solids separated from tap water before and after passage through columns of activated carbon

Solids from	Component						
	Calcite, $CaCO_3$	Goethite, α-FeOOH	Lepidocrocite, γ-FeOOH	Quartz, SiO_2	Cuprite, Cu_2O	Magnetite, Fe_3O_4[a]	Small-grained or amorphous[b]
Original water	Extremely strong	Very strong	Very strong	Strong	Medium strong	Moderately Weak	Not observed
Column A	Extremely strong	Very strong	Very strong	Strong	Medium strong	Not observed	Very strong
Column B	Medium strong	Not detected	Not observed	Not observed	Weak	Moderately weak	Extremely strong

[a] maghemite (γ-Fe_2O_3) could not be distinguished from Fe_3O_4, but is less likely to form in tap water at ambient temperature; [b] a broad, featureless band between 15 and 40°.

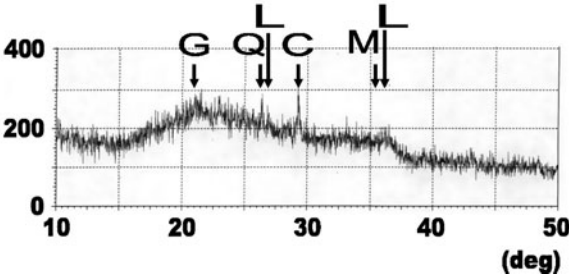

Fig. 2. X-ray diffractogram of solids separated from tap water on the coarse activated carbon column (column A). G = Goethite, Q = Quartz, L = Lepidocrocite, C = Calcite, and M = Magnetite.

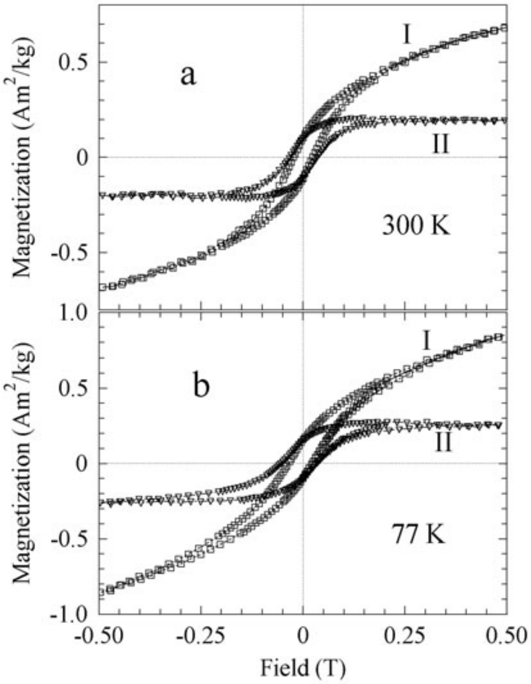

Fig. 3. Magnetic hysteresis measurements on solids recovered from Column B. (a) (at room temperature), and (b) (at liquid nitrogen temperature). The figure contains both the experimental data(I), and the results after subtraction of the superparamagnetic component (II).

Column B is assumed to be in the form of superparamagnetic magnetite particles. In addition, SEM measurements showed that the majority of the solids in the tap water used in the experiments with activated carbon consisted of fine particles below the resolution of the SEM, that is, below about 2 μm. EDS spectroscopy of the same solids indicated that iron was the most abundant of the inorganic elements present, in agreement with the results of the chemical analysis, and that it was distributed uniformly over the assemblage of fine particles. It should be noted that neither magnetization measurements nor XRD are effective in distinguishing between magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), particularly when the measurements are performed on low-weight samples. Both of these iron oxides have been identified as corrosion products in water supply systems [4]. Thus, the magnetic particles identified in the present study may have consisted of either or both of these species.

4. Discussion

The results of the experiments with the activated carbon, summarized in Tables 2 and 3, show that the coarse carbon removed the majority of the iron, copper, and lead from the tap water, but a sizeable fraction (13–19%) of these elements was left in the water. However, subsequent passage of the same water through the fine carbon resulted in complete removal of these elements from the water. Fine carbon also removed from the water a large fraction of other elements, such as zinc and nickel, from water which had previously passed through the coarse carbon column.

Activated carbon made from coconut shells has a very high external surface area. Thus, both the coarse activated carbon (Fisher Scientific 05-685A) and the fine activated carbon (Fisher Scientific 06-690A) used in the present study were stated by the vendor to have a specific surface area of approximately 1,000 m^2/g. The large surface area accounts for the high capacity of coconut shell carbon for sorbing ionic and molecular species. (For instance, the capacity for sorbing iodine, known as the iodine number, is approximately 1,000 mg I_2 per g of carbon). It should be taken into account, however, that these values for the specific surface area are based on the adsorption of very small molecules, most commonly N_2. The effective surface area available for the adsorption of such molecules predominantly consists of the internal surface area, that is, the area of open pores, with only a small contribution from the outer surface area. This accounts for the measured surface area being largely independent of the particle size. Compared with other types of activated carbon, the product made from coconut shell has a high ratio of micropores (having a diameter of about 2 nm) to macropores. This accounts not only for the high sorption capacity for small molecules, but also for the fact that the coarse and fine activated carbons are stated to have the same specific area. As explained previously, the large abundance of micropores causes their contribution to overall surface area to be predominant, and thus, the grain size is not expected to affect the sorption capacity of coconut shell carbon as long as the sorbed species has a diameter of <2 nm. However, as the size of the sorbed species increases, first the micropores and then pores of larger diameter become unavailable for sorption. As a result, the relative contribution of the outer grain surface to sorption grows, and fine-grained materials can be expected to exhibit higher capacity for sorption and to become more effective with respect to sorption of large molecules and particles, especially in cases where the affinity of the adsorbed species to the adsorbing surface is not very high [19]. As mentioned previously, the results of the magnetic measurements shown in Fig. 3 indicate that the magnetite nanoparticles have a diameter of at least about 4.5 nm. (Magnetite nanoparticles also tend to form clusters that increase their effective size [20]). Thus, they are too large to be absorbed in the pores of the activated carbon, and they are mostly adsorbed on the surface of the activated carbon grains. This accounts for the greater efficiency of fine carbon, which has a much larger outer surface area, in removing magnetite nanoparticles from the water. Goethite and lepidocrocite, in contrast with magnetite, have high surface activity in aqueous media [9,21] because, unlike magnetite, they carry significant surface charge in aqueous media due to the presence of hydroxyl groups. Accordingly, goethite and lepidocrocite are effectively removed from the water even when coarse activated carbon is used. This is demonstrated by the XRD and magnetization data, which provide evidence for the conclusion that, unlike the two FeOOH species, magnetite tends be concentrated on the fine carbon column.

Both iron oxyhydroxides [4,9] and nanoparticles of iron oxides, such as magnetite [10–12], can, in their turn, adsorb other species. Goethite, for instance, is known to be an effective sorbent of Pb [22,23], Cu [24,25], and As [21,25]. Magnetite nanoparticles have been recently reported to adsorb Cd(II) [26], As(III), and As(V) [14], Cu(II) [27], and, to a lesser extent, Cr (VI) [27]. Even though the present study did not include measurements on As, we know that the superparamagnetic particles that were removed contained arsenic, as was shown in the previous paper [16]. As detailed in the previous paragraph, magnetite is adsorbed effectively only by fine activated carbon, while goethite and lepidocrocite can be removed even upon using coarse activated carbon. These two observations can be used to account for the finding that the removal of species such as Fe, Zn, Cu, Pb, Al, and Ni on the coarse carbon filter was incomplete, despite the fact that, based on the data in Table 2, the total amount of these species was only about 0.1 g, or 2 mmol, while the volume of the column was 44 mL. These species, however, were completely or largely removed from the water after passing the water through the fine carbon column which was placed downstream form the coarse carbon column and had the same volume as the preceding column. Based on the discussion in the previous paragraph, this finding can be readily attributed to these metal species being associated with two distinct forms of iron. Goethite and lepidocrocite and the Zn, Cu, Al, and Ni associated with them are readily removed by coarse carbon, while magnetite nanoparticles and the fraction of the Zn, Cu, Al, and Ni associated with them require the use of fine activated carbon for effective removal.

The use of a coarse carbon column upstream of the fine carbon column increases the effectiveness of the system because the coarse carbon column removes the goethite and lepidocrocite particles, which account for more than 80% of the iron-based particles, and can also protect the fine carbon column against fouling or clogging by other solids such as silica, aluminosilicates or organic matter. Thus, the configuration consisting of a coarse carbon bed followed by a fine carbon bed is preferable to a single bed of fine carbon.

The slight increase in the concentrations of Ca, K, and Si observed upon passing the tap water through the activated carbon columns (see Table 2) can be attributed to leaching of these soluble species from the activated carbon, in which they are present as significant impurities (see Table 1).

The present study confirms that fine particles consisting of, or coated by, iron oxyhydroxides or nanoparticles of magnetite (and, probably, maghemite), which are formed by the spalling off of corrosion products from drinking water pipes, can take up contaminants such as Pb and Cu. (Arsenic can also be adsorbed on such particles). Contaminant uptake on such particles may have serious health implications. Furthermore, as water flows through the pipes, the ratio of fine particles to coarse particles increases, facilitating the transport of such particles to the consumers' homes or public facilities. The removal of contaminated nanoparticles of corrosion products from drinking water poses greater difficulties than the removal of monomeric metal ions, which can be accomplished by ion exchange, or the removal of coarse particles, which can be removed using filtration through ordinary filtration media requiring only a small pressure gradient. Ultrafiltration and reverse osmosis are intended to remove suspended particles in the nanosize range, but because of the high cost of these techniques, the coarse carbon/fine carbon sequence discussed above may provide an economically viable alternative, especially in cost-sensitive applications such as supply of water to individual households.

5. Conclusions

Both iron oxyhydroxides and nanoparticulate iron oxides, in particular magnetite (and/or maghemite), produced as a result of pipe corrosion are present as a large fraction of the total solids in tap water. These species can take up significant amounts of the contaminants in the water (such as Pb and Cu) and transport them to consumers. The results of the study demonstrate that the use of a column of coarse activated carbon to remove the iron oxyhydroxides and the contaminants that they carry, followed by a column of fine activated carbon to remove iron oxide nanoparicles and associated contaminants, can be highly effective in eliminating contaminants from drinking water.

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