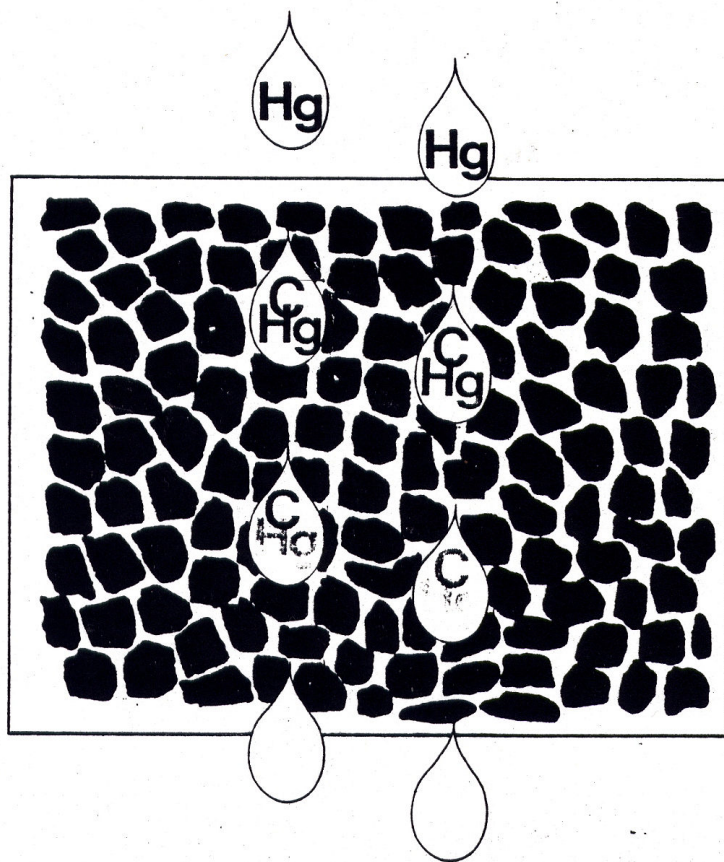


Removal of Mercury From Drinking Water Using Activated Carbon

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and John T. O'Connor



A paper contributed to and selected by the JOURNAL, authored by Leon Thiem (Student Member, AWWA), doctoral student, Diane Badorek, (Student Member, AWWA), doctoral student, and John T. O'Connor, prof. and chairman, Dept. of Civ. Engrg., (Active Member, AWWA), all of Univ. of Mo., Columbia, Mo.

Rigorous controls on levels of mercury in drinking water and increased monitoring mandated by the Safe Drinking Water Act urged an investigation into practical treatment techniques for lowering mercury levels in water. Aqueous solutions of mercury were treated by various combinations of activated carbon, EDTA, tannic acid, citric acid, and calcium. Samples close to neutral pH allowed the most effective treatment; quite small additions of tannic acid-dramatically increased treatment success, as did progressively higher concentrations of calcium ions.

Because of its many unique properties, mercury has found widespread use in diverse applications ranging from dental fillings to thermometers. A major industrial user of mercury has been the chloralkali producers. This industrial user cannot recover all of the mercury that is used during production, and one estimate is that about 0.1 kg of mercury will be lost from the process for every 900 kg of chlorine that is produced.¹ Another major use of mercury is in specialized batteries which have long lives and constant voltages. Although batteries account for most of mercury's usage in the electrical industry, many electrical instruments such as switches and relays utilize mercury's conductive properties. Large amounts of mercury are used in the Chemical Oxygen Demand test to prevent interferences in measuring the strength of organic wastes. Organic mercurials are extremely effective pesticides and thus have been used in marine

paints and on agricultural seeds to prevent infestations. Still another source of potential mercury pollution is the burning of coals, which contain an average of 0.3 mg/l of mercury.² During coal combustion, a portion of the mercury is volatilized and enters the atmosphere as a vapor that will dissolve in rain. Eventually it will return with the rainfall and enter the aquatic ecosystem as a toxic pollutant.

This widespread use of mercury leads to the problem of accidental contamination of natural ecosystems from careless or poor disposal methods. Unfortunately, mercury's many beneficial uses are linked to its potent and possibly fatal toxic properties. Because of these health concerns, the levels of mercury in drinking waters must be extremely low, and are stringently controlled by regulatory agencies. In addition, the provisions of the Safe Drinking Water Act require a significantly increased national program of water-quality monitoring. As part of the surveillance program, numerous water utilities which have not previously monitored trace metals will have to initiate such a program. It is possible that at least a few of the more than 40 000 public water supplies in the US will find quantities of toxic trace metals in excess of those which are allowed under drinking-water standards.

If the concentrations of metals found are not grossly in excess of the established limits, and if alternate water sources are not readily available, what means will be available to water utilities for removing quantities of toxic trace metals which are present in concentrations ranging from two to five times those allowable under the drinking water standards? Such concentrations would require 50 to 80 per cent removal in conventional water-treatment plants that are modified to enhance metals removal. The object of this study is to explore means for removing trace concentrations of mercury II from drinking water supplies, utilizing existing treatment facilities.

Earlier studies of trace metals removal had indicated that activated carbon could be effective in removing trace metal cations from municipal wastewater effluent.³ However, carbon was found to be inconsistent and only partially effective in removing trace metals from synthetic waters or raw water supplies low in organic matter.⁴⁻⁶ From these results, it was hypothesized that organic complexation of trace metals may enhance their removal by activated carbon. The current study was designed to observe this phenomenon in a more systematic fashion, within the constraints of practical applicability in water-treatment plants.

Experimental Procedure

A number of simplifying assumptions were made to limit the number of possible experimental variables. First, the quantity of metal present was set at five times the allowable limit stated in the current drinking-water standard. This amounts to an initial concentration of 10 $\mu\text{g/l}$ for mercury. As a result, the processes under study must consistently remove at least 80 per cent of the mercury for the treatment to be considered acceptable. It was also assumed that the mercury would not be complexed to any great extent by organic materials before the addition of the chelating agents utilized in the study.

Activated carbon was applied in powdered form because this method would provide flexibility in treatment and could easily be incorporated into existing treatment plant schemes. Only one grade of carbon* was employed in the testing program. Because this grade of carbon is granular in nature, only that portion which

passed a #200 sieve and thus would be equivalent to a powdered grade was utilized. While carbon dosages from 10–100 mg/l were studied, it was assumed that 40 mg/l might be a practical maximum dosage for continuous use.

Batch tests were conducted using 100 ml aliquots of test solution. The test solution, unless otherwise noted, was essentially a distilled water solution of $\text{Ca}(\text{HCO}_3)_2$ with the alkalinity adjusted to approximately 2 meq/l, and a Hg(II) concentration of 10 $\mu\text{g/l}$ added as the chloride salt, HgCl_2 . The analysis was facilitated by the addition of the radiotracer Hg-203 which exhibits the same chemical behavior as the nonradioactive form of mercury.

At the start of each run, activated carbon was added to the reaction bottles in dosages ranging from 10–100 mg/l and the pH was adjusted by adding a sufficient quantity of either nitric acid or sodium hydroxide. The bottles were then placed on a shaker mechanism and agitated for a period of 1 hr to provide contact between the carbon and the mercury solution. After 1 hr, samples were taken from the reaction bottles and passed through a 0.45 μm membrane filter to simulate conventional sand filtration. The amount of mercury that was removed from solution by adsorption onto the carbon was then measured radiometrically, with corrections made to account for any removal that might have been observed due to adsorption onto the cellulose acetate filter or glassware.

Mercury speciation is affected by such factors as redox potential, pH, and the type and concentrations of ligands present in solution. Under the conditions of the testing medium, the redox potential was equivalent to that of a natural, well-aerated stream and the ligands included chloride, hydroxide, nitrate, and bicarbonate. Of these ligands, only chloride and hydroxide combine to any appreciable extent with mercury II. At the pH values of 7–9 that were used for testing purposes, the principal form of mercury would be $\text{Hg}(\text{OH})_2$ which is a dissolved, uncharged molecular species.⁷ A soluble chloride complex was not formed due to the low concentration of chloride present in the test solution.

For a portion of the tests, an organic complexing agent such as EDTA, tannic acid, or citric acid was added to the test solution in the reaction bottles prior to the addition of the powdered activated carbon. These particular complexing agents were chosen on the basis of their potential chelating ability, their ability to be adsorbed onto the carbon, and their occurrence or potential acceptability for addition to drinking-water supplies.

Results

Influence of pH. The results of the studies to determine the removal of mercury by adsorption onto powdered activated carbon are shown in Fig. 1. In these tests, only the effect of the addition of carbon in the presence of varying hydrogen ion concentrations was investigated. No chelating agents were added at this time.

From these curves, it can be seen that less than 30 per cent of the 10 $\mu\text{g/l}$ solution of mercury was removed at a carbon dosage of 10 mg/l at pH 7. This would seem to indicate that the activated carbon that is currently being added to water supplies in the range of 5 mg/l to control tastes and odors may be accomplishing little in the way of mercury removal. Much higher dosages with longer contact periods would be required. As the dosage was increased to 40 mg/l, nearly 60 per cent removal of mercury was achieved. Only when 100 mg/l of carbon was applied to the test solution did the residual concentration approach the established drinking-water standard.

*Calgon Filtrasorb 400

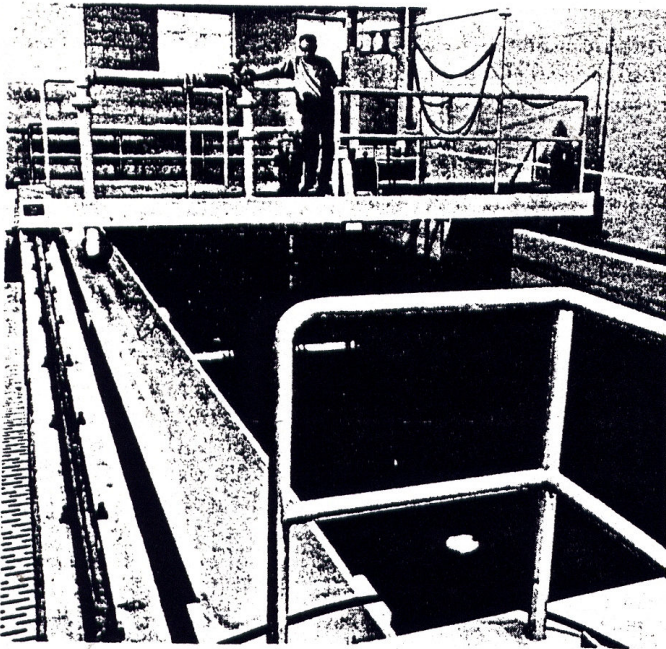


Photo courtesy Koppers Co., Pittsburgh, Pa.

It may be possible to extrapolate the author's results to use of full-scale carbon beds.

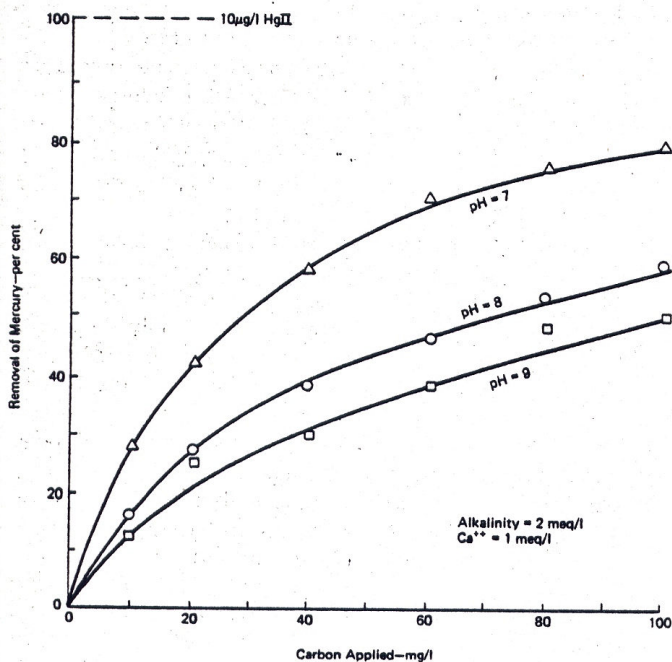


Fig. 1 Influence of pH on the Removal of Mercury II From Aqueous Solution by Powdered Activated Carbon.

Removal also appears to be quite sensitive to pH. Roughly twice as much mercury was removed at pH 7 as at pH 9. Increasing hydroxyl ion concentration evidently inhibited mercury adsorption onto the powdered activated carbon. At no time was the water standard met under these conditions.

Addition of EDTA. Pre-treatment with three concentrations of EDTA was studied: 0.19 mg/l, 1.9 mg/l, and 19 mg/l. A concentration of EDTA equal to 19 mg/l corresponds to 10^{-1} times the concentration of divalent ions in solution, or in other words $M(EDTA)/M(Ca^{++} + Hg^{++}) = 0.1$.

When no EDTA was added to the test solution, and when a quantity equal to 1.9 mg/l was added to the test solution, the results were numerically similar. The resulting curve is essentially the same as that presented in Fig. 1 which represents the removal of mercury by powdered activated carbon alone at pH 7.

When concentrations of 0.19 and 19 mg/l of EDTA were tested, the removals observed in both instances were very similar but not so close as to be indistinguishable. At these concentrations of EDTA slight improvements in the removal of mercury were noted, with a 5-15 per cent increase observed depending upon the carbon dosage applied. During these tests, the drinking-water limit for mercury was met but only at carbon dosages of 80 mg/l and higher.

It was expected that the addition of EDTA would enhance the removal of mercury by forming a metal-organic complex with it; in this form it should have been more effectively adsorbed by the activated carbon. Judging from the data, this does seem to have occurred but no explanation could be found for the variation in removal that resulted from the three different EDTA dosages that were applied. The addition of 19 and 0.19 mg/l of EDTA produced equally good mercury removals, while the addition of 1.9 mg/l of EDTA produced no improvement over what could be removed by carbon alone. Further study is planned employing a radioactive form of EDTA to explain these unexpected results.

Addition of tannic acid. Of the three chelating agents that were studied, tannic acid proved to be the most effective in enhancing removal. Concentrations of 1 and 10 mg/l, which are within the range of occurrence in natural waters, were used for testing purposes. In Fig. 2, the results that were obtained at pH 7 are presented; while the effect of adjusting the pH to 8 is shown in Fig. 3.

At pH 7, the addition of 1 mg/l of tannic acid to the test solution dramatically improved the removal of mercury by the activated carbon. Over 70 per cent removal was achieved by a carbon dose of 20 mg/l, while 40 mg/l of activated carbon resulted in 85 per cent removal, reducing the concentration of mercury below the drinking-water standard. The most startling results were obtained at the low carbon dosages of 10-20 mg/l where the removals were nearly double those values observed when only carbon was reacted with the test solution. Although the higher concentration of 10 mg/l of tannic acid also showed increased removals over those produced by activated carbon only, it appeared to suppress mercury removal when compared to the data for the 1 mg/l concentration of tannic acid. Although not shown, the removal of mercury was further suppressed when a concentration of 50 mg/l of tannic acid was present. This would point to the existence of an optimum dose of chelating agent that, when exceeded, would begin to interfere with the removal mechanism, possibly by covering the available reaction sites on the carbon surface.

When the pH of the test solution was raised from 7 to 8, the removals that could be achieved were reduced considerably, although the curves still maintained the same relative positioning

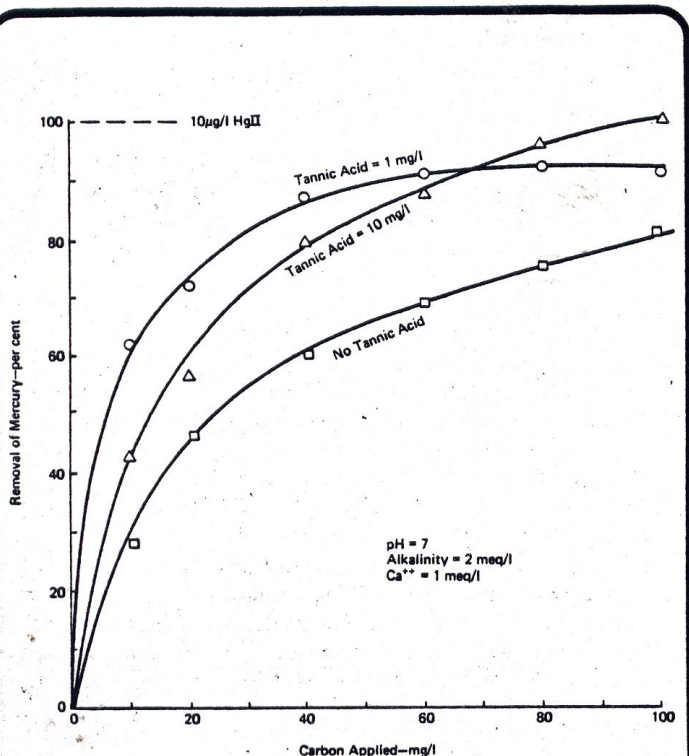


Fig. 2. Influence of Tannic Acid on the Removal of Mercury II From Aqueous Solution by Powdered Activated Carbon

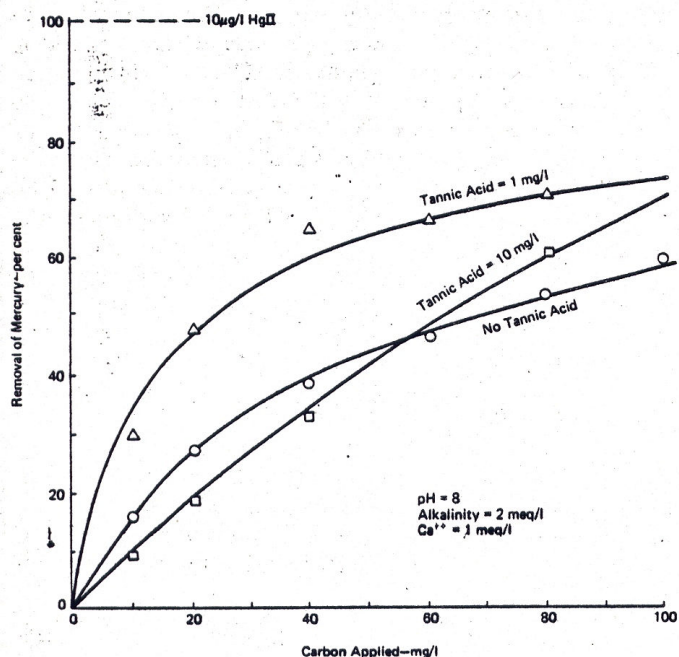


Fig. 3. Influence of Tannic Acid on the Removal of Mercury II From Aqueous Solution by Powdered Activated Carbon

with respect to each other that was observed at pH 7. The greatest removal of mercury at pH 8 again occurred in the presence of the 1 mg/l concentration of tannic acid, but these values were only equal to the removals that were accomplished by adsorption onto carbon alone at pH 7.

Addition of citric acid. Little or no improvement in mercury removal resulted from the addition of 0.01 mg/l and 0.1 mg/l concentrations of citric acid at pH 7. Thus it can be concluded from the data that citric acid applied at these concentrations does not substantially hinder or enhance mercury removal on activated carbon.

The data obtained at pH 8 show slightly more significant results. As was observed in earlier tests, the removal efficiency of the activated carbon decreases with increasing pH. Approximately a 30 per cent reduction in capacity was noted for the case when no citric acid was added to the test solution and the pH was raised from 7 to 8. However, with increasing pH, the stability of the metal chelates tends to increase, and this may account for the higher removals of mercury that were observed. In this case, the addition of citric acid increased the percentage of mercury removed by the activated carbon but not enough to equal the degree of removal obtained by the carbon alone at pH 7.

Influence of calcium. The influence of calcium ion concentration on the removal of mercury from aqueous solution by powdered activated carbon is shown in Fig. 4 and 5. All of the tests were conducted at pH 8 and the calcium ion concentration was varied from 50–200 mg/l. The condition under which 50 mg/l of calcium was present in solution was analogous to contacting activated carbon with the original test solution adjusted to pH 8.

It was felt that calcium might compete with mercury for adsorption sites on the carbon surface or form a complex with the chelating agents and thus reduce the amount of chelate available to form a complex with mercury. So it was expected that the addition of calcium would inhibit the removal of mercury by activated carbon. Surprisingly, this was not the case.

Figure 4 demonstrates how increasing the calcium ion concentration from 50 mg/l to 100 mg/l enhanced mercury removal by a small but readily measurable degree. As the concentration was raised to 200 mg/l, a similar result was noted over the entire range of carbon dosages that were tested. From 10–20 per cent higher removals could be achieved in this manner.

The addition of 1 mg/l of tannic acid to these high calcium ion solutions produced even greater removals of mercury by carbon. Although each curve of Fig. 5 shows only a slight, progressive improvement over that which precedes it, this family of curves is positioned relatively higher on the graph when compared to Fig. 4. Depending upon the amount of calcium ion in solution and the carbon dosage applied, removals increased from 15 per cent to as much as 50 per cent. The greatest increases that were observed occurred at carbon dosages in the range of 10–40 mg/l.

The experimental results show that the addition of calcium ion, or calcium ion in conjunction with tannic acid, results in increased removals of mercury onto powdered activated carbon. This may occur because the calcium ion in solution reacts with the surface groups on the activated carbon in such a way that new adsorption sites are created in the process. Thus, the higher the concentration of calcium ion in solution, the greater the number of new sites that can be produced. The end result is the observed increase in capacity for the adsorption of mercury and the mercury complex. Further investigation into the mechanism of trace metal removal on activated carbon might employ carbon-14 labelled chelating agents to determine the concurrent removal of the organic substances as well as the mercury.

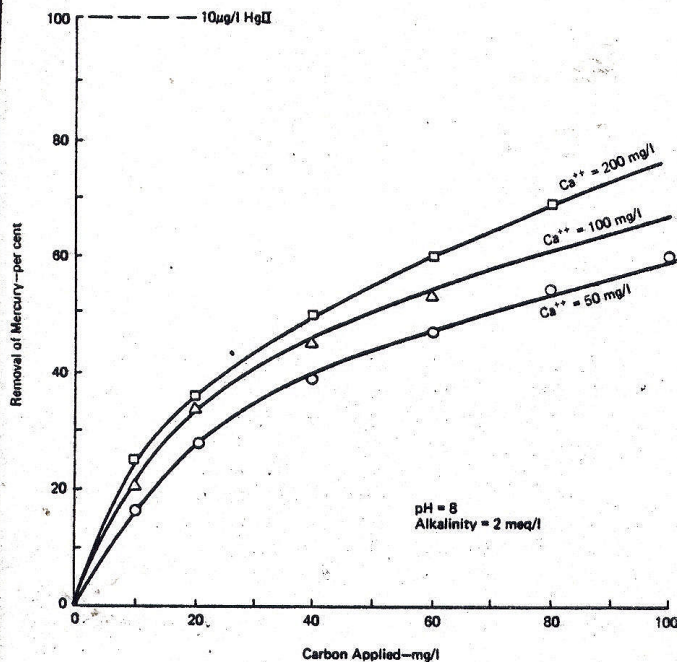


Fig. 4. Influence of Calcium on the Removal of Mercury II From Aqueous Solution by Powdered Activated Carbon

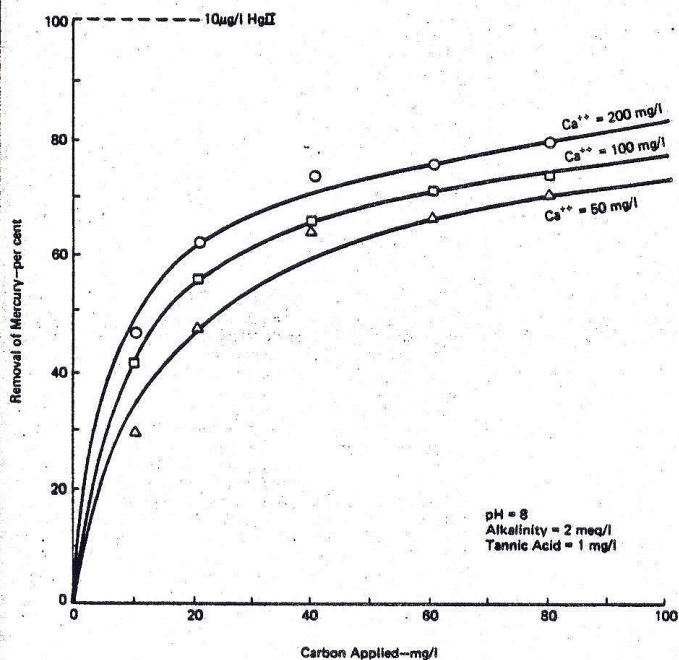


Fig. 5. Influence of Calcium and Tannic Acid on the Removal of Mercury II From Aqueous Solution by Powdered Activated Carbon

Conclusions and Summary

Adsorption of mercury II by powdered activated carbon is one possible alternative for the removal of this metal from drinking-water supplies. The degree of removal is dependent upon the pH of the medium, with a noticeable decrease in the adsorption of mercury as the pH is increased. Within the range of pH of natural waters, the best results were observed around neutrality.

The addition of chelating agents such as EDTA or tannic acid prior to contact with activated carbon measurably improved the removals that were noted when only carbon was added to the system. Concentrations as low as 0.02 mg/l of EDTA or 1 mg/l of tannic acid increased removals from 10-30 per cent, depending upon the carbon dosage that was applied and the pH of the system. While tannic acid proved to be the most promising chelating agent that was studied, citric acid had the least effect and did not appear to either enhance or inhibit the adsorption of mercury by activated carbon. Once again, the greatest removals occurred when the pH of the system was adjusted to 7.

Calcium ion exhibited an effect on the removal of mercury similar to that of the chelating agents that were tested. As the calcium ion concentration was raised from 50 to 200 mg/l, mercury removals were seen to increase 10-20 per cent over those obtained by carbon alone. When 1 mg/l of tannic acid was added to the system in conjunction with the higher levels of calcium ion, mercury removals nearly doubled at the lower range of carbon.

The results of these tests indicate that the presence of chelating agents will enhance the removal of mercury from drinking water using powdered activated carbon as an adsorbent. Calcium, which is naturally present in many water supplies, may have a similar effect. Further studies are planned to determine the optimum conditions for the removal of these metals from water sources which are found to have concentrations of mercury in excess of those allowed under the new drinking water standards. Perhaps equally important, these studies may provide added insight into the interaction between metals and naturally-occurring organic substances which may either enhance or inhibit the removal of metals by coagulation, filtration or adsorption.

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