QUANTIFICATION OF THE CATALYTIC EFFECT OF ACTIVATED CARBON ON THE REMOVAL OF MONOCHLORAMINE

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Introduction

Activated carbon has been identified as a catalyst for monochloramine decomposition to ammonia and nitrogen. A significant amount of work has been performed examining the relationship between process variables, such as carbon particle size, empty bed contact time, and monochloramine concentration,[1,2,3] and the carbon quantity that is required for complete reaction. However, these studies were performed without examining the effect of the carbon catalytic properties. Using hydrogen peroxide decomposition as an indicator of the activated carbon catalytic characteristics, an improved prediction of the carbon catalyst performance for monochloramine decomposition will be investigated.

Experimental

These studies were conducted using bituminous and sub-bituminous based activated carbons and also Centaur® carbon, which is a catalytically enhanced bituminous based carbon. All of the carbons were 20x50 mesh. The laboratory system consisted of a series of one inch internal diameter glass columns through which the monochloramine solution was pumped using a Masterflex pump. Column connections were made with Norprene tubing. The feed water to the columns was prepared by blending tap water (Robinson Township Municipal Authority) and a monochloramine stock solution (300 mg/L) such that the influent concentration averaged 5 mg/L. The monochloramine stock solution was prepared by combining one liter of a 1.5 g/L ammonium chloride solution with one liter of a solution containing 1.25 g sodium carbonate and 12.5 mL of sodium hypochlorite. All reagents were Fisher certified.

The monochloramine analyses were performed using primarily the Hach method 8167 with DPD pillow reagents and the Hach DR2000 spectrophotometer for total chlorine. Periodic accuracy measurements were performed using purchased solution standards and following the standard additions method provided by Hach. Influent chloramine concentrations were validated by the Syringaldazine (FACTS) method for free chlorine, Standard Methods 4500-Cl, H.

Results and Discussion

Figure 1 shows that activated carbons can be differentiated based upon the reaction of monochloramine.

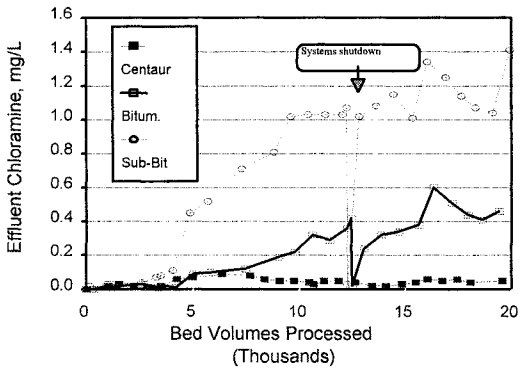

Figure 1. NH2Cl Decomposition - Effect of Carbon

The above data were generated at a contact time of two minutes, with an average influent concentration of 5 mg/L. Obviously, the catalytic Centaur carbon significantly outperformed the standard bituminous and sub-bituminous carbons. While the data in Figure 1 stops at 20,000 bed volumes, the Centaur carbon continued to operate through 88,000 bed volumes or five months without exceeding the treatment objective of 0.1 mg/L, at which point the experiment was terminated.

Komorita and Snoeyink[1] predict that a usable bed life for a 20x50 granular carbon would be about 55,000 bed volumes for an influent monochloramine concentration of 2.8 mg/L in Champaign-Urbana, IL tap water. However, in the current studies the volume of water that can be

treated before exceeding the 0.1 mg/L level is only 4,000 and 6,000 bed volumes for the two standard carbons. While the influent concentration in the current study is somewhat higher, and the tap water is somewhat different, the performance change of 4,000 to 6,000 bed volumes to 55,000 bed volumes processed cannot be related solely to the water characteristics. Rather, the catalytic properties of the activated carbon used to treat the water are critical and need to be specified.

One method of measuring the catalytic activity of activated carbon is through the use of hydrogen peroxide decomposition.[4] In this patented test, 0.25 g of pulverized activated carbon react with 0.42 moles of hydrogen peroxide inside of a dewar. The solution is buffered to a pH of 7 to compensate for any pH change that may occur because of the inherent carbon characteristics. The temperature rise due to the decomposition of the hydrogen peroxide is measured and the elapsed time to reach the maximum temperature is determined. The initial temperature rise is very fast but then slows considerably once the temperature is within 80 to 90% of the maximum temperature. To increase the precision and accuracy of the test, the 75% point is chosen for the catalytic activity measurement. The time to reach 75% of the maximum temperature is recorded as the t¾ time. The maximum temperature typically observed ranges between 40 and 60°C.

The three activated carbons that were used to develop the curves in Figure 1 had different catalytic activities and the greater the catalytic activity (lower t¾ time) the greater volume of water that can be treated until the 0.1 mg/L monochloramine treatment objective is exceeded. As summarized in Table 1, the three activated carbons have catalytic activities ranging from 8 minutes to 40 minutes, as measured by the t¾ time.

Comparison of the catalytic activity measurement with the water volume treated shows that the volume increases as the catalytic activity increases. In the same laboratory study as in Figure 1 but at a 45 second empty bed contact time, the subbituminous based carbon was able to treat 500 bed volumes, and the standard bituminous based carbon could treat 1,000 bed volumes of water. Enhancement of the catalytic activity allows 3,000 bed volumes of water to be treated.

In much the same way, the reaction rate constant shows a significant increase as the catalytic activity increases. Scaramelli and DiGiano[2] noted that steady state occurred at about 140 hours of operation and that the monochloramine decomposition is pseudo first order. At an equivalent operating time in the current work, the first order rate constant changes as the catalytic activity changes. For example, the rate constant increases from 0.15 to 0.22 L/g-hr as the t¾ time changes from 40 to 30 minutes. Further increasing the catalytic activity to 8 minutes results in another significant increase in the rate constant to 0.34 L/g-hr.

Carbon	t¾ (min)	BV treated @ 45 sec.	k (L/g-hr)
Centaur	8	3,000	0.34
Std. Bituminous	30	1,000	0.22
Subbituminous	40	500	0.15

Table 1. Effect of Catalytic Activity Measurement on Water Volume Treated and Reaction Rate Constant

Conclusions

Improvements in the ability to predict the performance of activated carbons in the catalytic decomposition of monochloramine are possible by measuring the catalytic activity of the carbon. The use of the t¾ time test has been shown to be a measure of the carbon catalytic activity and an indicator of carbon performance. Thus, enhancing the natural catalytic activity increases the reaction rate constant and allows for a greater volume of water to be treated when monochloramine decomposition is the objective.

References

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4. Hayden, R.A. and Matviya, T.M., United States Patent 5,470,748, Nov. 28, 1995.