

IMPROVED GRANULAR ACTIVATED CARBON FOR THE STABILIZATION OF WASTEWATER PH

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Keywords - pH stabilization, Granular activated carbon, Carbon oxidation

ABSTRACT

Laboratory studies have identified the cause of the pH rise, which occurs during water treatment with activated carbon, as an interaction between the naturally occurring anions and protons in the water and the carbon surface. The interaction can be described as an ion exchange type of phenomenon, in which the carbon surface sorbs the anions and corresponding hydronium ions from the water. These studies have shown that the anion sorption and resulting pH increase is independent of the raw material used for the activated carbon production, e.g. bituminous or sub-bituminous coal, peat, wood or coconut. Also, the pH excursions occur with virgin, reactivated, and acid washed granular carbons. Current pH control technologies focus on adjustment of the wastewater pH prior to discharge or recycle of the initial effluent water until the pH increase abates. However, improved water pH control options have been realized by altering the carbon surface through controlled oxidation rather than the water chemistry or extended preprocessing at the treatment site.

INTRODUCTION

Many times, the start up of granular activated carbon adsorption systems for the control of organic contaminants in wastewater exhibits unacceptable increases in the adsorber effluent pH. This increase can result in an effluent pH exceeding NPDES permits. Experience shows that the duration of the pH increase ranges from several hours to several days, during which time several hundred bed volumes of water can be discharged with a pH in excess of 8.5 to 9, which are typical high limits on discharge pH.

Historically, the methods used in the remediation of the high pH effluent were to treat the effluent with acid to lower the pH, to backwash the system for extended periods of time, or to recirculate the water until the pH rise naturally abated. Obviously, an incentive exists to remediate the problem with methods other than the extensive and expensive ones mentioned here. As a result, a program was begun to identify the cause of the pH excursions and provide a cost effective remediation to the problem.

EXPERIMENTAL

The activated carbons used in this experimentation were both virgin and reactivated, acid washed and non acid washed, and produced from a wide variety of raw materials. The water used in the experimentation was either tap water from the Robinson Township Municipal Authority, a suburb of Pittsburgh, or ultra pure Milli-Q Plus water (Millipore Corp. Bedford, MA). Additionally, when examining specific anion effects, the sodium salt of sulfate, chloride, or nitrate was added to the Milli-Q water. These salts were Fisher ACS grade or equivalent.

pH measurements were performed following Standard Methods⁸. Anion analyses were performed with a Dionex Model 14 Ion Chromatograph (Dionex Corp. Sunnyvale, CA). Cation analyses were performed using atomic absorption spectroscopy.

The experimental apparatus consisted of a one inch ID x 12 inch L Pyrex glass column through which the water was pumped upflow with a Masterflex peristaltic pump and tygon tubing. Each carbon was boiled in Milli-Q water for 15 minutes, cooled to room temperature, and then transferred to the column. The water flow rate provided approximately 7.5 minutes empty bed contact time (EBCT), and discrete samples were collected for analysis. For the anion specific experiments, the water was prepared in a seven gallon, glass carboy.

The oxidized carbons were prepared at both high and low temperature with air as the oxidant.^{4,5,6} Carbon pH measurements on both oxidized and non-oxidized carbons were performed by gently stirring 25 g of carbon in 100 mL of a sodium sulfate solution (80 mg sulfate/L) for 30 minutes. This procedure is referred to as the modified contact pH.

RESULTS AND DISCUSSION

Effect of Water Quality

The extent and duration of the pH excursion depends upon the water quality. Using Filtrasorb 200 as the test carbon in this simulation, the water was varied from tap to Milli-Q water. Figure 1 shows that tap water from Robinson Township, PA yields a pH rise up to 10. With the Milli-Q water, the excursion is very limited, i.e. 40 bed volumes when the pH drops below 8.5. However, the pH excursion can occur with Milli-Q water through the introduction of any of a number of anions. Shown in Figure 1 is the effect of sulfate addition on the pH spike. Adding 80 mg/L of sulfate causes the pH spike to return and the pH profile closely matches that of tap water. (Throughout this discussion, 8.5 pH is chosen as the reference point for a pH excursion.)

The type of anion does not have a significant effect on the excursion, and concentration only affects the pH profile at low anion concentrations. Table 1 highlights the excursion that occurs as the anion concentration and anion changes. When the anion changes from sulfate to chloride to nitrate, the impact of the anion is negligible with the pH peak occurring around 10 and the excursion lasting about 400 BV. Only at very low concentrations does the pH spike become muted. The loading of the anions ranges from 3.3 to 4.3 mg/L after treating 400 bed volumes of water. Cations were not removed by the carbon.

Effect of Carbon Type

A pH excursion has been shown to be independent of the raw material and whether or not the carbon is acid washed. Figure 2 shows that whether the carbon is prepared from bituminous or sub-bituminous coal, coconut, wood, or peat each carbon exhibits an increase in pH when the carbon is brought on line. This same conclusion results when the carbon is acid washed and also following reactivation.

Hypothesized Mechanism

It is believed that the pH excursions are a function of the activated carbon surface that results from the high temperature activation or reactivation process. Huang¹ broadly classifies activated carbons as H or L types of carbon. In these broad categories, an H-type carbon, produced at high temperature in a reducing atmosphere, adsorbs strong acids while L-type carbons, produced by surface oxidation, adsorb strong bases. Thus, adsorption of "acid groups" as witnessed by Snoeyink² may be responsible for upsetting the water equilibrium. This adsorption may actually be protonation of pyrone type surface oxides (Leon y Leon³) or other structures on the carbon surface. Following protonation, the surface is charge neutralized with the sulfate, chloride, or other anions which may be present in the water. In absence of these ions, the neutralization of the surface occurs with the hydroxide ions that result from hydrolysis of water which initially yielded the protons. It may actually be more accurate to say that the anions (sulfate, chloride, etc.) exchange with the hydroxide ions following protonation; however, additional testing will be required to conclusively determine the mechanism.

pH Stabilization with Oxidized Carbons

An effective remediation of the pH increases is accomplished through the controlled oxidation of the activated carbon surface, prior to treating the water, which alters the carbon surface to stabilize the effluent water pH. Two methods have been developed to achieve this. First, an elevated temperature oxidation^{4,5} provides surface oxides that inhibit the ion exchange phenomenon and stabilize the pH. Likewise, a low temperature oxidation also effectively stabilizes the water pH⁶.

When carbon prepared by either of these methods is exposed to water, the excessive pH rise in the effluent water is eliminated. Figure 3 shows that both the high temperature and low temperature oxidized pH stable carbons can keep the effluent water pH at or below the target pH of 8.5. Further, effluent water pH stabilization can be accomplished for both the synthetic water prepared with Milli-Q water plus sulfate and also tap water, which had an initial pH of 7.8. The two stabilized pH profiles were developed with virgin carbon (Milli-Q plus 80 mg/L sulfate) and reactivated carbon (tap water) which demonstrates that the oxidation processes are applicable to both virgin and reactivated carbons. The modified contact pH of the oxidized virgin carbon was 7.4 while the oxidized reactivated carbon had a modified contact pH of 8.5. Finally, Carr and Farmer⁷ demonstrated that pH stabilized carbons can be implemented easily in full scale systems.

Surrogate pH Stable Carbon Test

A modification has been made to a standardized pH test to predict whether a carbon will exhibit a significant pH rise. The standard test contacts carbon with deionized water. With this test, most carbons will have a contact pH between 6 and 8. However, by adding sulfate to the deionized water, greater pH changes can occur, and the test can be used to predict whether the carbon will

cause a rise in the effluent water pH. Table 2 shows that carbons with a modified contact pH above about 9 will exhibit a pH increase. Also, with the exception of the wood base carbon, as the modified contact pH decreases, the duration of the pH increase generally decreases.

SUMMARY AND CONCLUSIONS

Stabilization of the effluent water pH has been demonstrated through the use of oxidized granular activated carbons. This oxidation can be accomplished at both low and elevated temperatures through the use of air, oxygen, or other suitable oxidants and is applicable to both virgin and reactivated carbons. Prediction of the ability of a carbon to stabilize the effluent water pH is also possible through the use of the modified contact pH test.

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Table 1. Effect of Anion and Anion Concentration on Effluent pH Profile

Anion	Concentration mg/L	Maximum pH	pH Excursion Duration Bed Volumes	Anion Loading mg/g GAC
Sulfate	80	10.5	360	4.3
Chloride	18	10.2	420	3.3
Nitrate	5.3	9.8	>410	3.9
Sulfate	1	9.4	220	0.73

Duration of the pH spike represents volume of water treated until pH \leq 8.5
 Water used was Milli-Q water spiked with the referenced amount of anion
 Anion loading is represented as mg anion/g GAC after treating 400 bed volumes

Table 2. Modified Contact pH and Extent of pH Excursion

Activated Carbon	Modified Contact pH	pH Excursion Duration (Bed Volumes)
Bituminous	10.4	350-400
Sub-bituminous	10.4	350
Peat	11.1	460
Coconut	10.3	200-250
Bituminous-acid washed	9.8	200-250
Wood	9.6	550
Reactivated bituminous	10.6	400
pH Stable	8.2	0

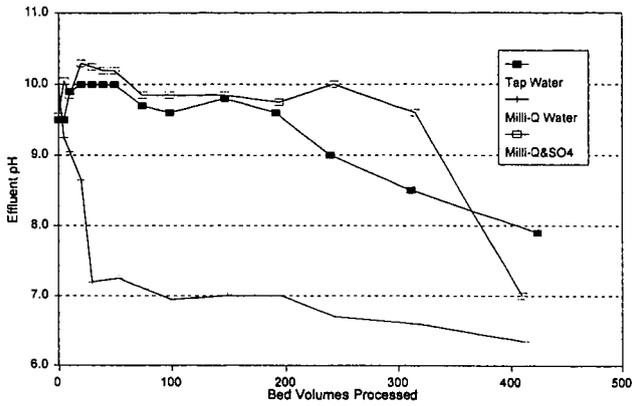


Figure 1. Effect of Water Quality on pH Profile - Bituminous Carbon

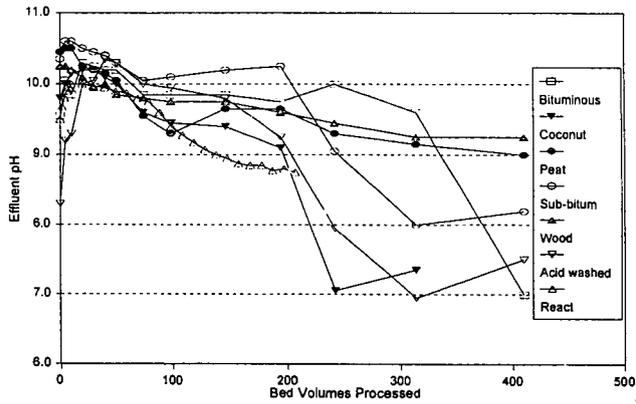


Figure 2. Effect of Carbon Raw Material on pH Profile - Milli Q Water & Sulfate (80 mg/L)

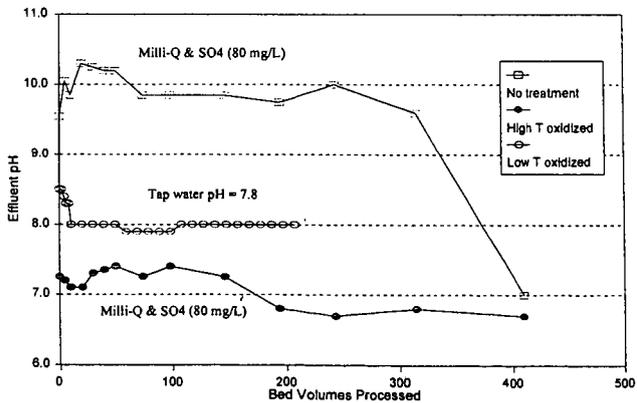


Figure 3. Effect of Oxidized Carbon on pH Profile - Bituminous Carbon