Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

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To cite this Article Reed, Brian E.(1995) 'Identification of Removal Mechanisms for Lead in Granular Activated Carbon (GAC) Columns', Separation Science and Technology, 30: 1, 101 — 116
To link to this Article: DOI: 10.1080/01496399508012216
URL: http://dx.doi.org/10.1080/01496399508012216

SEPARATION SCIENCE AND TECHNOLOGY, **30**(1), pp. 101–116, 1995

Identification of Removal Mechanisms for Lead in Granular Activated Carbon (GAC) Columns

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ABSTRACT

In an earlier study the removal of lead by a granular activated carbon (GAC) column was increased by over 600% when the carbon [Hydrodarco 4000 (HD4000), Norit Americas, Inc.] was contacted with a 0.1 N HNO_3–0.1 N NaOH rinse. Hypothesized removal mechanisms were adsorption, surface preceipitation, and pore precipitation. In this work a series of experiments were conducted on samples of the virgin and acid–base rinsed carbon to determine their acid–base behavior, pH_{zpc}, and Pb removal ability. If adsorption was a dominant removal mechanism, then significant differences in these parameters for the virgin and acid–base rinsed carbons would be expected. The strong acid–base rinse did not significantly alter the acid–base behavior, pH_{zpc}, or the Pb removal ability compared to virgin HD4000. Thus, it appears that the dramatic increase in metal removal by the regenerated GAC columns was not caused by an increase in the number or type of adsorption sites but was due to the precipitation of Pb on the carbon surface or in the carbon pore liquid. Future research efforts will focus on the modeling of Pb removal in GAC columns using precipitation as the primary removal mechanism.

INTRODUCTION

In the past, granular activated carbon (GAC) columns have been used exclusively for the removal of trace quantities of organic compounds. Despite the fact that several researchers have demonstrated the ability of activated carbon to remove heavy metals from aqueous waste streams (1–8). The majority of these studies were conducted in the batch mode.

Recently, Reed and Arunachalam (9) demonstrated that GAC columns were effective in removing lead and cadmium from solution and that an increase in carbon pH during the regeneration step dramatically improved the metal removal ability of the GAC column. A possible metal removal mechanism put forward by Reed and Arunachalam (9) included sorption (physical and chemical), surface precipitation, and pore precipitation.

STUDY OBJECTIVES

If GAC columns are to be accepted as a treatment process for metal-bearing waste streams and if modeling the removal of metals by GAC columns is to proceed, then the operative removal mechanism(s) must be identified. With this in mind, the objective of this study was to gather information to determine to what extent metal removal is due to adsorption and precipitation (surface or pore).

SELECTED BACKGROUND INFORMATION

Adsorption of metal cations onto hydrous solids is strongly dependent on the pH of the solution (10). The dependence of metal adsorption on pH is due in part to the amphoteric nature of hydrous solids and the solution chemistry of the metal ion. For cationic metals in a ligand-free system, adsorption generally increases with solution pH. The fraction of metal ions removed from solution increases from near zero to 1 over a narrow pH range. The metal removal curve versus pH is referred to as a "pH-adsorption edge."

pH-adsorption edges represent metal–carbon behavior in the batch mode at equilibrium. If activated carbon is to gain acceptance as a metal removal process, its effectiveness must be demonstrated in the column mode. Reed and Arunachalam (9) investigated the removal of lead and cadmium by the granular activated carbon HD4000 (Norit Americas, Inc.). A flow rate of 2 gpm/ft^2 was used, and the packing density was approximately 0.33 g/cm^3. Dead volume in the columns was not determined. Breakthrough curves [normalized effluent metal concentration versus number of bed volumes (BV) treated] are presented in Fig. 1 for 10 mg/L Pb. Also presented in Fig. 1 is the column effluent pH versus bed volumes treated. The column was subjected to four treatment cycles. For Run 1, approximately 50 BVs were treated prior to breakthrough (defined as $C_e/C_0 \approx 0.03$). Following the completion of Run 1, the column was regenerated using an acid–base rinse consisting of contacting the column with 10 BVs of 0.1 N HNO_3 followed by 10 BVs of 0.1 N NaOH. The acid was used to lower the pH of the carbon so that desorption could occur while

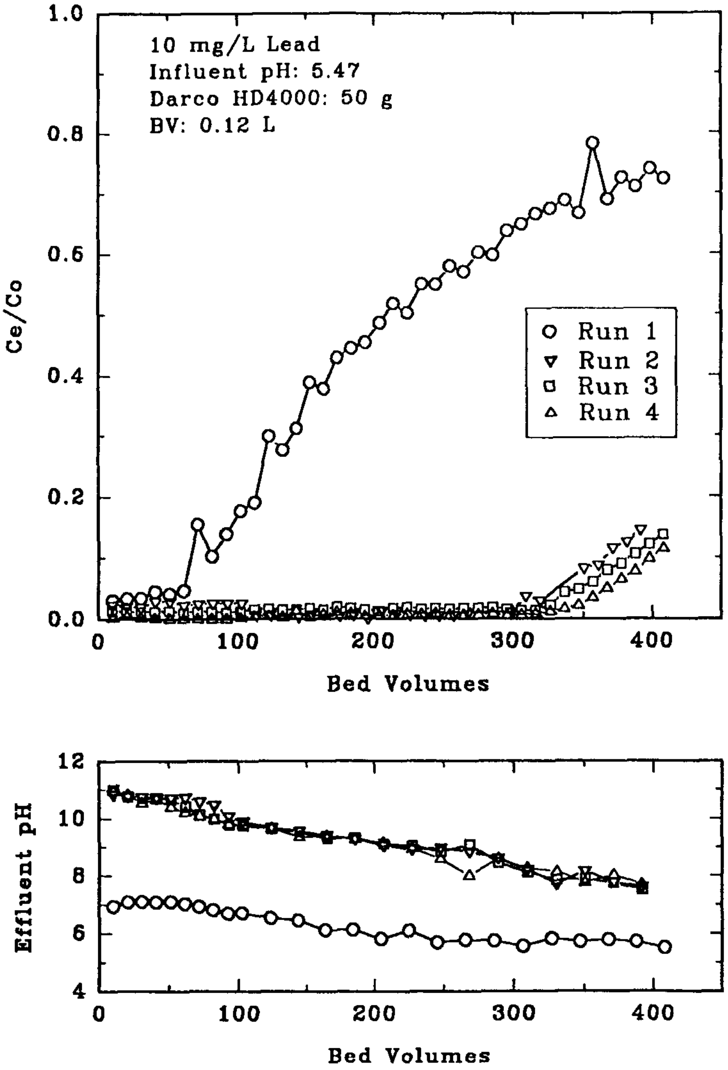

FIG. 1 Breakthrough curves for HD4000 and 10 mg/L Pb.

NaOH was used to raise the column pH prior to the next treatment run (removal increases with increasing pH). For Run 2, approximately 300 BVs were treated prior to breakthrough, representing a 600% increase over the virgin carbon results (i.e., Run 1). The increase in lead removal was attributed to the increase in column pH. The effluent pH of the virgin column ranged from about 7 at the beginning of the run to below 6 at the completion of the run. The effluent pH of the regenerated carbon at the start of the run was greater than 11 and decreased to about 8 by the end of the run. The increase in column pH was caused by the base rinse step of the regeneration procedure. Following Run 2, the operational cycle (treatment–regeneration) was repeated two additional times. The results from Runs 2 through 4 are similar, strongly indicating that the regeneration procedure did not have an adverse affect on column performance. In Fig. 2 the Pb concentration in the acid regenerant versus bed volumes of regenerant is presented for the 10 mg/L Pb experiments. The majority of Pb was desorbed from the carbon after about four bed volumes of acid regenerant. The concentration of lead in the base regenerant was negligible. Similar results were observed for 10 mg/L cadmium and HD4000.

The effect of column pH on metal removal is more apparent when one views the breakthrough curve for 50 mg/L Pb that is presented in Fig. 3. The rapid rise in effluent lead concentration corresponds directly with the decrease in the column pH. In Fig. 4 the Pb concentration in the acid

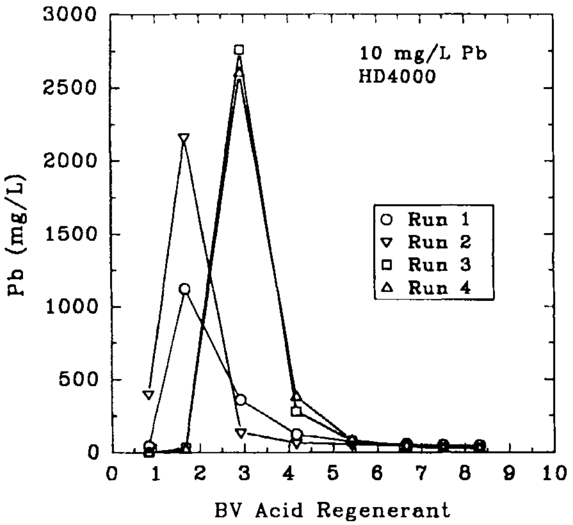

FIG. 2 Pb concentration in the acid regenerant versus bed volumes for 10 mg/L Pb.

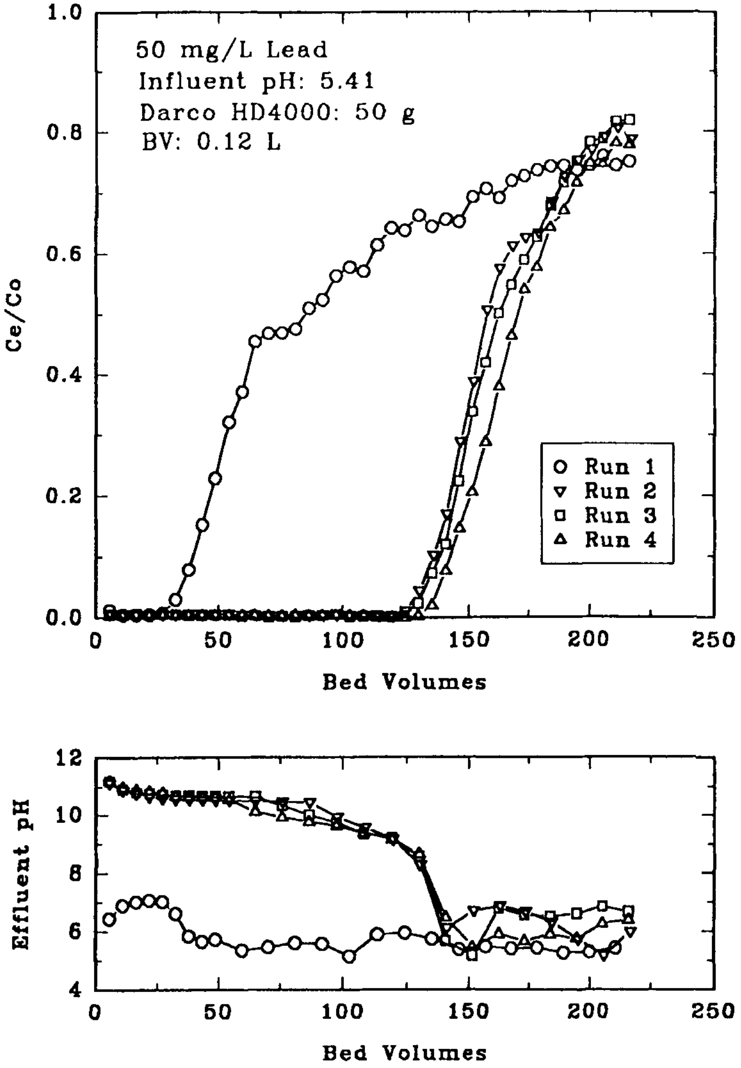

FIG. 3 Breakthrough curves for HD4000 and 50 mg/L Pb.

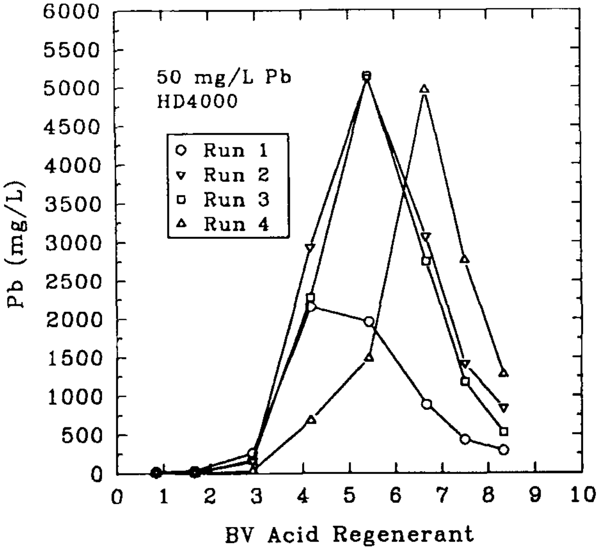

FIG. 4 Pb concentration in the acid regenerant versus bed volumes for 50 mg/L Pb.

regenerant versus bed volumes of regenerant is presented for the 50 mg/L Pb experiments. After about eight bed volumes of acid regenerant there was still a significant amount of lead in the regenerant, indicating that there was still lead remaining in the column. However, the peak lead concentration occurred between about five and seven bed volumes of regenerant. The lead remaining in the column did not adversely affect subsequent column performance (see Fig. 3). Similar results were observed for 50 mg/L cadmium and HD4000.

Possible causes for the increase in metal removal by the regenerated carbon include: 1) an increase in the number of surface sites, 2) precipitation of the metal on the carbon's surface, 3) precipitation of metal in the carbon's pore liquid, and 4) swelling of the carbon resulted in more pores available for interaction with the metal ion. Reed and Nonavinakere (11) summarized the results of several researchers investigating methods to increase the number of surface sites on activated carbon by subjecting the carbon to an oxidizing environment (e.g., acid–base rinse). Reed and Matsumoto (2) reported that surface precipitation can occur about 1/2 to 1 pH units below the pH where solution precipitation would occur. With pore precipitation, the carbon acts as a "reservoir" for OH^-. The amount of metal removed by surface and pore precipitation is difficult to separate. The effect of carbon swelling was not investigated in this research.

EXPERIMENTAL DESIGN

To determine to what extent the increase in metal removal was due to adsorption or precipitation (surface or pore), the following experiments were conducted on virgin and acid–base rinsed HD4000: 1) acid–base titrations, 2($NaNO_3$ titrations, and 3) batch Pb removal isotherms as a function of pH (i.e., pH–adsorption edges). The carbon that was subjected to the acid–base rinse will be referred to as "pretreated carbon" and the acid–base rinse will be referred to as the pretreatment step.

Acid–base titrations of the carbon provides an estimate of the number of surface sites and of the amount of OH^- contained in the pores of the carbon. Inert salt ($NaNO_3$) titrations procide an estimate of the pH at the zero point of charge (pH_{zpc}). The pH_{zpc} is the pH at which the surface has a net zero charge. At pHs < pH_{zpc}, the surface has a net negative charge and at pHs > pH_{zpc}, the surface has a net positive charge. The pH_{zpc} is important in assessing the electrostatic behavior of the carbon–metal system and is an indicator of the type of sites present on the carbon surface. The pH–adsorption edges provides a relationship between Pb removal capacity, solution pH, and carbon concentration. If adsorption is the primary removal mechanism, then the increase in Pb removal observed in the GAC columns between Run 1 (virgin carbon) and Run 2 (acid–based rinsed carbon) should be accompanied by a noticeable change in surface behavior (i.e., the results from the acid–base and $NaNO_3$ titrations, and pH–adsorption edges for the virgin and pretreated carbons should be dramatically different). If the surface characteristics of the virgin carbon were not significantly altered by the acid–base rinse, then the increase in Pb removal during GAC column operation was most likely caused by precipitation (surface and pore).

MATERIALS AND METHODS

Carbon Preparation

Virgin and pretreated carbon were prepared in a similar manner. Characteristics of the virgin HD4000 (Norit Americas, Inc.) are presented in Table 1. Information in Table 1 was provided by Norit Americas, Inc. Unmodified HD4000 was placed in a column having an inner diameter of 2.5 cm and a length of 15 cm. Careful attention was paid to minimize the introduction of air bubbles into the column as this would affect the columnh hydrodynamics. For virgin carbon, the column was rinsed with deionized water until the conductivity was low. The pretreated carbon was rinsed with 10 BV 0.1 N HNO_3 followed by rinsing with 10 BV 0.1

TABLE 1
Characteristics of HD4000

Surface area (N_2 BET method), m^2/g	625
Slurry pH	5.2
Ash content, %	23
Molasses number	812
Iodine number	647
Mean pore radius, angstroms	29
Total pore volume, mL/g	1.04
Apparent density, g/mL	0.37
Particle density wetted, g/mL	1.4
Mean particle diameter, mm	1.09
Effective size	0.74
Uniformity coefficient	1.44

Particle size distribution, U.S. Sieves	%
+12	5.86
12 × 16	19.12
16 × 20	34.87
20 × 30	38.75
30 × 40	1.05
40 × 50	0.13
−50	0.23

N NaOH. Following the column rinsing step (either DI water or 0.1 N acid/base), the carbon was air-dried, then ground to pass a number 100 mesh sieve, and stored until needed.

Acid–Base Titrations

Four carbon slurries (50 mL), each containing 10 g/L of either virgin or pretreated carbon, were prepared. The ionic strength was adjusted to 0.1 N using $NaNO_3$. Two of the samples were titrated directly, one with 0.1 N NaOH and the second with 0.1 N HNO_3. The remaining two samples were filtered through a 0.45-μm filter, and the filtrate was saved and titrated with 0.1 N NaOH and 0.1 N HNO_3. The acid and base legs of the suspension titrations were combined, as were those for the filtrate titrations to produce a titration curve between approximately pH 3 and 11. A 0.1 N $NaNO_3$ solution was also titrated between pH 3 and 11. Titrations were carried out using a Tanager Scientific Systems IDG-8800 automatic titration system in conjunction with an IBM XT computer. An Orion Research combination pH electrode (Model #91-05) was used to monitor pH. Samples were closed to the atmosphere during titration by sealing the pH electrode and titration reactor connection with parafilm. The titrator was programmed to deliver a volume of titrant such that the change in pH for each addition was 0.15 pH units. A 5-minute period between additions of titrant was used. If the pH had changed more than 0.02 units during the last 30 seconds of the 5-minute period, the next aliquot of titrant was not added and the sample was allowed an additional 5 minutes to equilibrate. Equilibrium was observed to be rapid (less than 5 minutes), and omission of a titrant addition seldom occurred. Huang (12) recommended using a fast titration, 2 to 5 minutes between titrant addition, to minimize the effect of slow pH drift. NaOH was stored in a reservoir with a soda lime scrubber to prevent contamination by CO_2. NaOH was standardized using Standard Methods Procedure 401 (13). HNO_3 was standardized by titrating a known volume of HNO_3 with NaOH of known normality to pH 7. Titrations were carried out at 22°C.

$NaNO_3$ Titrations

Inert salt titrations of the carbons were conducted by adding sufficient quantities of concentrated $NaNO_3$ solution to 10 g/L of 10^{-3} N $NaNO_3$ carbon slurries so that the ionic strength changed from 10^{-3} to 10^{-2} and from 10^{-2} to 10^{-1} without introducing a significant dilution error ($<1\%$). Prior to the initial concentrated $NaNO_3$ addition, the pH of the carbon slurries were adjusted so that the initial pH ranged from approximately 3 to 11. After each $NaNO_3$ addition, the samples were shaken for 24 hours and the pH of the solution was recorded. The change in pH from the initial pH after each addition of $NaHO_3$ was calculated.

pH–Adsorption Edges

Lead pH–adsorption edges were conducted for a Pb concentration of 100 mg/L and carbon concentrations of 0, 0.1, 1, 3, 5, and 10 g/L. Experiments were conducted in the absence of carbon to determine the removal of Pb from solution by precipitation. A predetermined volume of Pb and $NaNO_3$ stock solutions and mass of 100 mesh carbon were added to a 1-L volumetric flask such that upon dilution to 1 L with distilled water, the desired ionic strength and lead and carbon concentrations were achieved. Fifty milliliter aliquots were withdrawn and placed in 75 mL Nalgene bottles, and varying amounts of either 0.1 N NaOH or HNO_3 were added to the individual samples for pH adjustment. The samples were sealed and placed on a mechanical shaker and agitated for 24 hours. At the end of the 24-hour period, the samples were removed, the pH measured, and samples were filtered and measured for Pb by atomic absorption spectrophotometry. Results were plotted as the fraction of lead removed versus solution pH.

RESULTS AND DISCUSSION

Acid–Base Titrations

Acid–base titrations for virgin and pretreated HD4000 are presented in Figs. 3 and 4, respectively. Also presented in Figs. 5 and 6 is the titration curve for a 0.1 N $NaNO_3$ solution. For the virgin carbon, the filtrate and 0.1 N $NaNO_3$ curves were almost identical, indicating that the amount of impurities washed from the virgin carbon was small. In contrast, the filtrate and 0.1 N $NaNO_3$ titration curves for the pretreated carbon were much different. A significant quantity of base as washed from the pretreated carbon during the filtration step. This OH^- was most likely loosely associated with the internal portion of the pretreated carbon and indicates the carbon's ability to act as a OH^- reservoir. There was a large difference between the pretreated and virgin carbon suspension titration curves. However, the difference is attributed to the OH^- that was transferred during the filtration step, not from a change in surface characteristics. If the filtrate curves are subtracted from the corresponding suspension curves, the difference between the acid–base behavior of the pretreated and virgin carbons is relatively small. For example, the milliequivalents

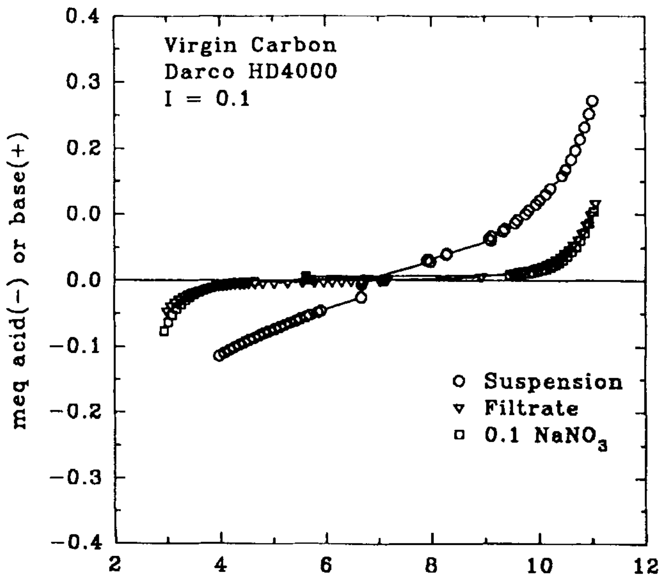

FIG. 5 Acid–base titration curves for virgin HD4000.

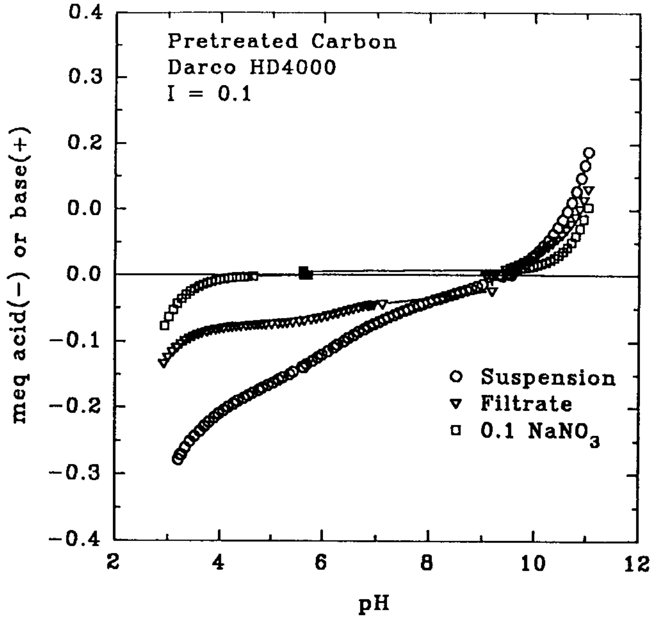

FIG. 6 Acid–base titration curves for pretreated HD4000.

of acid required to reach pH 4 was 0.21 for the pretreated carbon and about 0.195 for the virgin carbon. Thus, it appears that the acid–base rinse did not alter the surface of the carbon to the degree required to explain the dramatic increase in metal removal ability. The OH^- that resided in the carbon pores (as measured by the amount of OH^- in the pretreated carbon's filtrate) was available to precipitate with Pb. This hypothesis corresponds with the regeneration efficiencies observed during the GAC-Pb column runs. For the majority of the runs, the regeneration efficiency was less than 100%. If adsorption was the dominant removal mechanism, the number of surface sites (and Pb removal) should decrease with run number. However, if precipitation was dominant, metal removal would primarily be a function of the amount of OH^- present, and less than 100% regeneration would not affect removal unless the carbon pores were blocked by $Pb(OH)_2(s)$.

$NaNO_3$ Titrations

The titration of a hydrous solid with an inert salt gives an estimate of the pH_{zpc}. As the ionic strength increases, the change in pH of the carbon will be greatest at points away from the pH_{zpc}. At the pH_{zpc}, the change in pH should be zero, theoretically. Results from the $NaNO_3$ titrations are presented as the change in pH from initial value (delta pH) versus the initial pH in Figs. 7 and 8 for the virgin and pretreated carbons, respectively. The solid lines represent best fit equations to the experimental data. For both the virgin and pretreated carbons, the delta pH curves intersect the zero delta pH line in the range of pH 9 to 9.5. If the acid–base rinse altered the type of carbon surface sites, then the pH_{zpc} for the virgin and pretreated carbons should be different. Since this did not occur, it can be hypothesized that the carbon surface was not altered significantly, and the increase in metal removal was not due to an increase in the sorption behavior of the carbon.

pH–Adsorption Edges

In Figs. 9 and 10 the pH–adsorption edges for the virgin and pretreated carbons are presented, respectively. Also included is the Pb removal which would occur because of solution precipitation, [i.e., in the absence

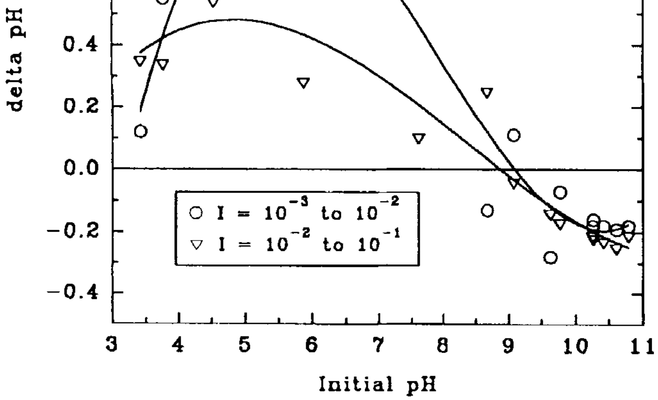

FIG. 7 Change in pH versus the initial pH for the $NaNO_3$ titration of virgin HD4000.

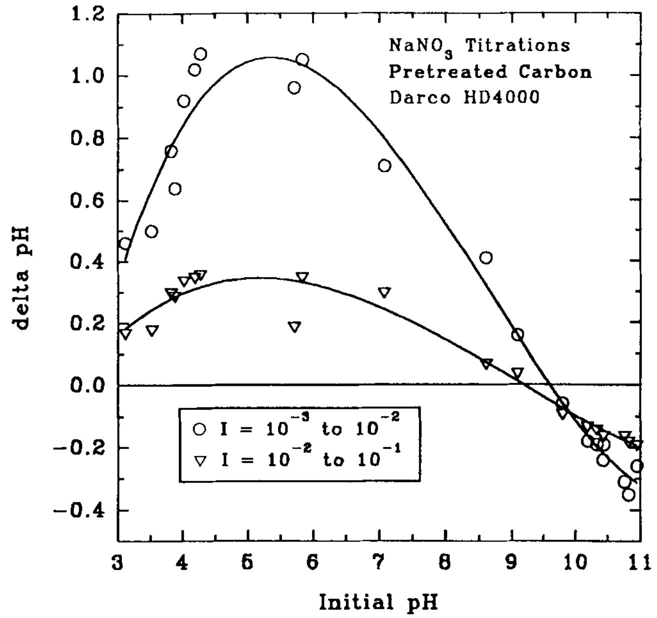

FIG. 8 Change in pH versus the initial pH for the $NaNO_3$ titration of pretreated HD4000.

of carbon as $Pb(OH)_2(s)$]. Both forms of carbon removed a significant quantity of lead prior to the pH at which precipitation occurred. The pretreated carbon was a slightly better adsorber of lead but not to the extent required to explain the increase in lead removal in the GAC column.

SUMMARY AND CONCLUSION

The strong acid–base rinse of carbon HD4000 did not significantly alter the acid–base behavior, pH_{zpc}, or the Pb removal ability compared to virgin HD4000. Thus, it appears that the dramatic increase in metal removal by the regenerated granular activated carbon (GAC) columns was not caused by an increase in the number or type of adsorption sites but was due to the precipitation of Pb on the carbon surface or in the carbon pore liquid. Future research efforts will focus on the modeling of Pb re-

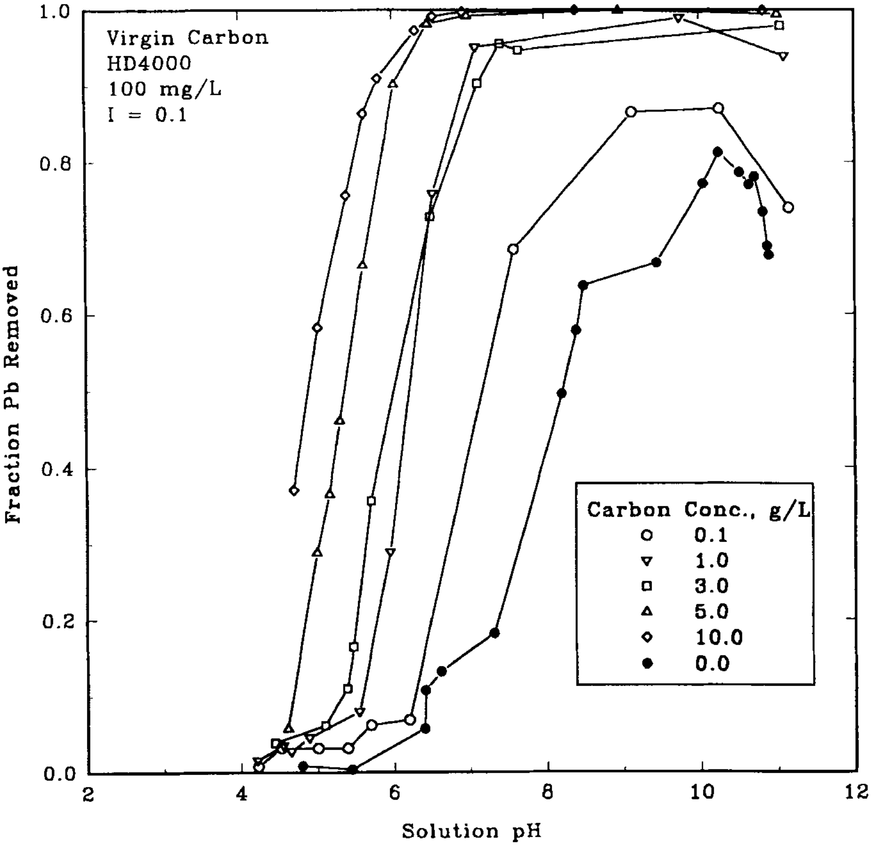

FIG. 9 pH-adsorption edges for virgin HD4000 and 50 mg/L Pb.

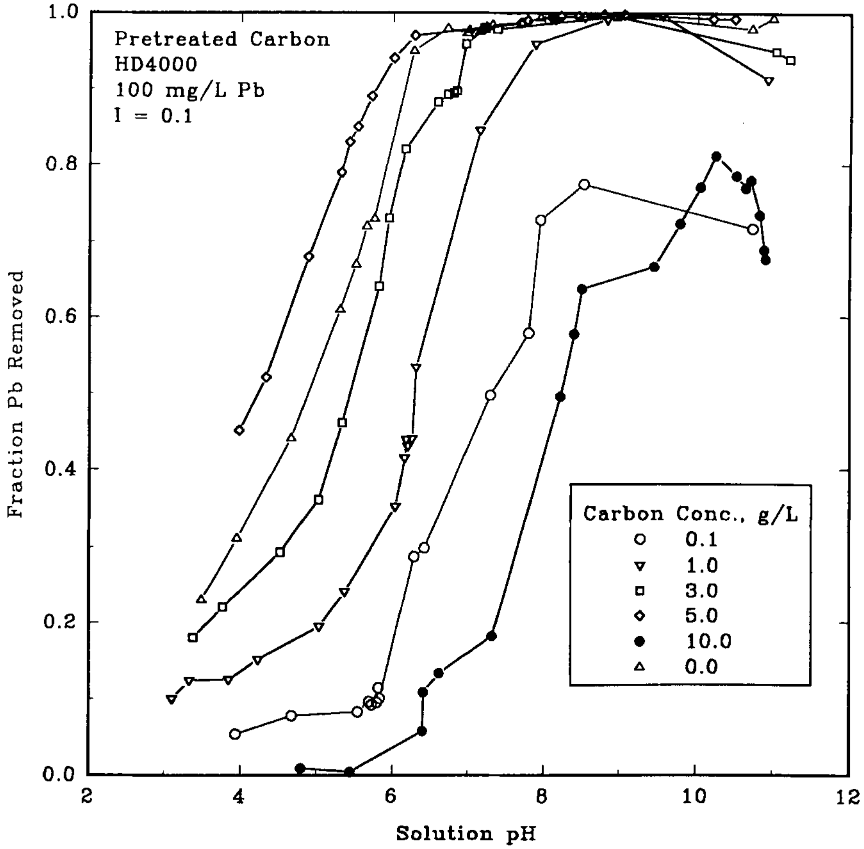

FIG. 10 pH-adsorption edges for pretreated HD4000 and 50 mg/L Pb.

moval in GAC columns using precipitation as the primary removal mechanism.

ACKNOWLEDGMENT

The author would like to acknowledge Norit Americas, Inc. for funding this research.

REFERENCES

1. B. E. Reed and S. K. Nonavinakere, *Sep. Sci. Technol., 27*(14), 1985 (1992).
2. B. E. Reed and M. R. Matsumoto, *J. Environ. Eng. Div. ASCE, 119*(2), 332 (1993).
3. C. P. Huang and F. B. Ostovic, *Ibid., 104*(5), 863 (1978).
4. C. P. Huang and E. H. Smith, "Removal of Cd(II) From Plating Waste Water by an Activated Carbon Process," in *Chemistry in Water Reuse*, Vol. 2 (W. J. Cooper, Ed.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 1981.
5. C. P. Huang and P. K. Wirth, *J. Environ. Eng. Div. ASCE, 108*(6), 1280 (1982).
6. M. O. Corapcioglu and C. P. Huang, *Water Res., 9*(9), 1031 (1987).
7. A. R. Bowers and C. P. Huang, *Prog. Water Technol. 12*, 629 (1980).
8. A. Netzer and D. E. Hughes, *Water Res., 18*(8), 927 (1984).
9. B. E. Reed and S. Arunachalam, *J. Environ. Eng. Div. ASCE, 120*(2), 416 (1994).
10. W. Stumm and J. Morgan, *Aquatic Chemistry*, Wiley, New York, 1981.
11. B. E. Reed and S. K. Nonavinakere, "Review of Activated Carbon Surface Acidity," in *American Chemical Society Specialty Series* (R. Peters and C. P. Huang, Eds.), In Press.
12. C. P. Huang, "The Surface Acidity of Hydrus Solids," in *Adsorption of Inorganics at the Solid-Liquid* (A. W. Anderson and A. J. Rubin, Eds.), Ann Arbor Science Publishers, Ann Arbor, Michigan, 1981.
13. American Public Health Association, *Standard Methods for the Examination of Wastewater*, 16th ed., Washington, D.C., 1985.

Received by editor September 16, 1993
Revised May 3, 1994