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Activated Carbon Process for Treatment of Wastewaters Containing Hexavalent Chromium

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July 1979

ACTIVATED CARBON PROCESS FOR TREATMENT OF WASTEWATERS CONTAINING HEXAVALENT CHROMIUM

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-CI) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

These studies were undertaken to develop a laboratory scale activated carbon process for treatment of hexavalent chromium containing wastewater. The mechanisms for removal of hexavalent chromium by activated carbon and the effects of various aqueous solution parameters on removal were examined, as well as different methods of regenerating the activated carbon.

Such information will be of value both to EPA's regulatory program (Effluent Guidelines Division) and to the industry itself in arriving at meaningful and achievable discharge levels. Within EPA's R & D program the information will be used as part of the continuing program to develop and evaluate improved and less costly technology to minimize industrial waste discharges. Besides its direct application to effluents from metal finishing industry, this technology may find application to treat metal-containing wastes generated by a host of other industries.

For further information concerning this subject the Industrial Pollution Control Division should be contacted.

David G. Stephan
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ABSTRACT

The removal of hexavalent chromium, Cr(VI), from dilute aqueous solution by an activated carbon process has been investigated. Two removal mechanisms were observed: hexavalent chromium species were removed by adsorption onto the interior carbon surface and/or through reduction to the trivalent state at the external carbon surface.

The effects of Cr(VI) concentrations, pH, carbon dosage and extent of mixing in the reaction vessel were studied in the batch mode and in continuous flow packed column experiments in the laboratory. The adsorptive capacity of the carbon and the rates of Cr(VI) adsorption and reduction have been determined.

Thermal regeneration of the exhausted carbon was examined, along with caustic or acid stripping solutions and a combined caustic-thermal process.

A case study was presented and the experimental data and rate expressions obtained from the data were used to evaluate the design variables (i.e., pH, carbon dose, Cr(VI) concentration and mixing in the reaction vessel). Several Cr(VI) treatment schemes were proposed, together with an economic analysis of each scheme.

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SECTION 1

INTRODUCTION

Recent concern over the presence and effects of heavy metals in the aquatic environment has prompted a significant national pollution control effort. Much emphasis has been on the re-evaluation of available removal techniques and the development of new processes for heavy metal removal from industrial and municipal wastewaters. Chromium has been a heavy metal of particular concern, due to its widespread industrial use and its chemical complexity. Chromium is a common pollutant found in a variety of industrial wastewaters, including those from the textile, leather tanning, electroplating and metal finishing industries. Chromium may be found in solution in various chemical forms. Textile and tanning wastes may contain either the hexavalent Cr(VI), or the trivalent Cr(III), chromium species; while electroplating and metal finishing wastes contain, primarily, the Cr(VI) species (1,2).

The toxicity and deleterious effects of chromium in natural waters are well documented. High concentrations of Cr(VI) species are lethal to marine organisms; while sub-lethal levels may retard fish reproduction and accumulate in fish tissues (3). The toxicity of Cr(III) is reportedly much less than Cr(VI); however, this may be due to the decreased solubility of the Cr(III) species compared to Cr(VI) (3,4).

Current practice in treatment of chromium laden wastewater has been oriented toward large scale operations. However, in the case of small plants, where economics prohibit extensive treatment, the wastewater often is simply discharged into the municipal sewage system (5). Much recent attention has been focused on the accumulation of heavy metals, including chromium, in municipal sludges. The extent of heavy metal accumulation in municipal sludge has provided a strong ground for challenging land application of municipal sludges on agricultural lands and thereby made sludge disposal an increasingly difficult problem (6). It is quite obvious that pretreatment of industrial wastewater before discharge to municipal sewers is necessary, if not currently mandatory, to alleviate this problem.

Conventionally, the most common means of removing heavy metals from wastewater is by chemical precipitation. In the case of hexavalent chromium which constitutes many anionic species, the Cr(VI) species must first be reduced to the trivalent form by reacting with sodium metabisulphite, sulphur dioxide, ferrous iron, or another common reducing agent at a pH of 2 to 3. The trivalent chromium may then be precipitated as the hydroxide, $Cr(OH)_3$, at optimum pH values of 8 to 9 (7). The precipitation process has not proven effective, because hydroxides form light precipitates which are difficult to

settle and dewater. Further difficulties arise when other heavy metals are present in solution with chromium and are to be removed simultaneously by co-precipitation. These difficulties result from the differences in the pH of minimum solubility for various metals. For instance, zinc has a minimum solubility at pH 9 to 10, nickel at pH 9.5 to 10.6, and cadmium has a minimun solubility at pH ranges from 11 to 12 (8,9,10).

Ion exchange has received limited application to industrial wastewater systems due to the destructive nature of most of these wastewaters on exchange resins, the poor selectivity for discrete ions in solution, poor loading capacities, high cost of exchange resins and high operating costs compared to other treatment systems (9,11).

Other methods, such as reverse osmosis, ion-flotation, electrodeposition, and solvent extraction have shown some experimental promise but have not fully demonstrated their effectiveness nor economic advantage for large scale operations (5,7,11).

Recently, activated carbon has shown promise for removal of inorganic heavy metals from wastewater. It is the intent of this investigation to develop and model the operating parameters which can be applied to a full-scale process for the removal of hexavalent chromium from a metal finishing related wastewater.

SECTION 2

CONCLUSIONS

Activated carbon is an effective adsorbent for removal of hexavalent chromium species from wastewater.

The maximum Cr(VI) adsorptive capacity of the carbon occurs at pH 2.5 and decreases rapidly between pH 2.5 and 7.1, primarily due to the decreasing electrostatic attraction between the positively charged carbon surface and the anionic Cr(VI) species in solution. The Cr(VI) adsorptive capacity decreases at pH < 2.5 due to the rapid reduction of the Cr(VI) species and the subsequent dominance of the cationic Cr(III) species at low pH.

The individual rates of removal due to reduction and adsorption were derived from laboratory experiments. The kinetic equations were:

$$-\left(\frac{dCr(VI)}{dt}\right)_{red} = \frac{2.4\ [HCrO_4^-][C]\ G\ [H^+]}{1.2 + 4.8 \times 10^4\ [Cr(III)] + 2.4 \times 10^5\ G\ [H^+][Cr(VI)]}$$

which is the rate of Cr(VI) reduction and:

$$-\left(\frac{dCr(VI)}{dt}\right)_{ads} = 2.9 \times 10^{-2}\ [H^+]^{0.2}\ [C][Cr(VI)]\ \{1 - \frac{\Gamma}{\Gamma_e}\}$$

is the rate of Cr(VI) adsorption. The carbon dosage, [C], is reported in (g/ℓ); $[HCrO_4^-]$, [Cr(VI)], and $[H^+]$ are all reported in (M) and the velocity gradient in the reaction vessel, G, is reported in (sec^{-1}).

The rate equations indicate that the ratio of reduction to adsorption of Cr(VI) species can be controlled by the pH and the mixing intensity in the reaction vessel.

For optimum removal, the carbon should be pre-washed with a solution at a pH approximating the pH of the wastewater to be treated.

Regeneration of the exhausted activated carbon is best accomplished by a caustic stripping solution. This also makes possible the recovery of Cr(VI) for reuse in a plating process.

Hexavalent chromium may be exclusively removed from solution through adsorption in a completely-mixed reaction vessel. By controlling the pH and

mixing in the vessel to inhibit the Cr(VI) reduction reaction at the carbon surface, the production of Cr(III) can be eliminated. However, the cost of operating such a system is somewhat higher than operating a packed carbon column.

Reduction of the Cr(VI) species cannot be eliminated from a packed carbon column, but a packed column is the most economical and simplest treatment scheme to operate. Therefore, if a separate carbon system can be devised to remove the Cr(III) produced, packed carbon columns would be an efficient, simple, economical, and environmentally compatible treatment process for the removal of hexavalent chromium species from wastewater.

SECTION 3

RECOMMENDATIONS

In this study, the parameters affecting the kinetics and extent of removal from synthetic Cr(VI)-containing wastewater were thoroughly examined. An actual wastewater will generally adhere to all of the kinetic equations, theories and treatment trends established in this report.

The ionic strength, Cr(VI) concentration, heavy metal constituents and various complexing agents found in an actual wastewater, may differ significantly from the laboratory prepared wastewater. These differences in solution components may alter the rate constants and extent of Cr(VI) removal for an actual wastewater. Therefore, a separate evaluation of each individual case is necessary.

The following procedures are recommended for designing an actual full scale activated carbon treatment process:

1. Obtain a typical sample of the wastewater to be treated (*ca* 50 gallons).

2. Perform several batch laboratory experiments at various adjusted solution pH's (one-liter samples with 2 grams carbon at initial pH 2.0 to 6.0 are recommended).

3. Adjust the wastewater to the desired pH and run several laboratory scale packed columns with different depths of carbon in each (at least 3 different depths) until breakthrough. The carbon should be pre-washed with clean water at the same pH as the adjusted wastewater. A flow rate of 2 gal/min-ft^2 is recommended.

4. The Cr(VI)-free effluent from the column experiments should be saved and batch experiments performed for removal of Cr(III), either by $Cr(OH)_3$ precipitation or carbon adsorption.

5. Exhausted carbon should be regenerated in batch experiments with various strengths of caustic solution to determine the percent concentration of the wastewater per strength of the caustic stripping solution. At least 10 grams of exhausted carbon per 200 mℓ of caustic solution should be used.

The experimental data obtained from the procedures outlined above can be evaluated and used in the graphs and equations presented in this report to determine:

a. the rate of reduction and adsorption of the Cr(VI) species;

b. the Cr(VI) adsorptive capacity of the activated carbon;

c. the amount of carbon needed for treatment;

d. the amount of Cr(III) which will be produced;

e. how often the carbon must be regenerated;

f. the volume of regenerant solution needed;

g. the cost of operating the system.

To improve this effort and establish a more complete set of criteria for operating an activated carbon system to remove total chromium from solution, the following are recommended:

1. A full scale system should be established in a small plant and operational parameters applied.

2. Further work should be done to examine various means of inhibiting the reduction of hexavalent chromium to trivalent chromium at the carbon surface.

3. More experimental work must be done on the adsorption and regeneration of an activated carbon process for the removal of trivalent chromium.

SECTION 4

ACTIVATED CARBON - BACKGROUND INFORMATION

GENERAL

Activated carbon has been widely used for the removal of taste and odor producing compounds and a variety of other organic pollutants, such as phenol or laundry surfactants, from water and wastewater (12).

Recently, the removal of inorganic pollutants and heavy metals by activated carbon adsorption has received considerable attention. Much of this work has been done in Japan, where heavy metals are a pressing concern. Kawashima and others reported significant removal of heavy metals from synthetic wastewaters using activated charcoal (13). Saito showed that the removal of heavy metals such as copper, cadmium, and ferric iron could be improved by treating activated carbon with sulfonate (14). In this country, Huang and Ostovic found a variety of commercial activated carbons to effectively adsorb cadmium, Cd(II), from dilute aqueous solution largely as a result of charge potential on the carbon surface (15).

CHROMIUM(VI) AND CHROMIUM(III)

Use of activated carbon to remove chromium(VI) from water is a recent endeavor. Toyokichi reported that chromates are effectively removed from wastewater by passing wastewater containing chromates through a column packed with platinum black catalyst-impregnated activated carbon. One Kg of activated carbon was mixed with 1 mℓ of platinum black colloid, containing 0.001 mg Pt/ℓ and 1 gm pure H_2SO_4. The platinum black catalyst-impregnated activated carbon (50 ℓ) was packed in a column and then wastewater containing 100 ppm chromate was passed through the column at 1 m^3/hr. The resulting wastewater contained less than 0.1 ppm chromate (16). A similar research work was conducted by Tagashira, et al., who found that by mixing 200 mℓ $K_2Cr_2O_7$ solution (534 ppm Cr) with 5 g powdered coconut shell charcoal (100-200 mesh 15%, 200-325 mesh 15%, and < 325 mesh 70%) and heating in an autoclave at 200°C for 30 minutes, can reduce the Cr(VI) concentration to 0.01 ppm (17).

Huang and Wu studied the removal of chromium(VI) by calcinated charcoal and found that removal was most significant at low pH and low initial Cr(VI) concentrations (18). They also postulated that $HCrO_4^-$ ions are the major species being removed, as shown by the following reactions:

$$C_xO + HCrO_4^- + H_2O = C_xO_4Cr^+ + 2\ OH^-$$

or

$$C_xO_2 + HCrO_4^- + H_2O = C_xO_5Cr^+ + 2\ OH^-$$

Seto and Tsuda reported that by mixing a 50 mℓ Na_2CrO_4 (10%) solution, with initial pH being adjusted to < 3, with 5 g activated carbon in a flask for 2 hrs at 25°C, the CrO_3 adsorption by the activated carbon was 39.7% and 3.3%, respectively, for final pH values of 3 and 7 (19).

Nagasaki, by heating lignite with 14% HNO_3 acid for 13 minutes, demonstrated that chromic acid ions were effectively removed (20). By passing a wastewater containing chromic acid (100 ppm), with pH being adjusted to equal to or lower than that of chromic acid, through an activated carbon column for 100 hrs, Nagasaki and Terada reported that the effluent contained neither Cr(VI) nor Cr(III) (21). After passing 1350 ℓ of water the effluent pH went up to 7 and contained 0.5 ppm Cr(VI). Ten liters of 25% HCl solution was then passed through the column to regenerate the column by dissolving the reduced Cr(III). The column was reused for another 100 hrs without breakthrough.

An EPA supported work, conducted by Landrigan and Hallowell, also demonstrated that activated carbon can be used by many small plating plants to relieve the chromium burden on municipal sewage systems (22).

Very recently, Yoshida, et al., studied the adsorption of Cr(VI) and Cr(III) onto activated carbon as a function of pH and the amount of total Cr and Cr(VI) eluted from activated carbon at pH 4-6.5 (23). They reported that Cr(VI) is readily adsorbed on activated carbon as anionic species, such as $HCrO_4^-$ and CrO_4^{-2}, while Cr^{+3} ion is scarcely adsorbed on activated carbon. They also observed that in acidic solution, Cr(VI) is easily reduced to Cr(III) in the presence of activated carbon. The adsorbed Cr(VI) species was elutable with NaOH (> 0.1 N) or with 1 N HCl solution.

Huang and Wu studied the effect of pH on Cr(VI) and Cr(III) under acidic conditions and in the presence of activated carbon (24). Kim reported that reducing reaction can be suppressed by adjusting the proton concentration to become equal to that of the hexavalent chromate, or to maintain a Cr(VI) system predominated by $HCrO_4^-$ species (25). Although a similar statement has been made by Nagasaki, et al.,(21) no such finding was observed in this study.

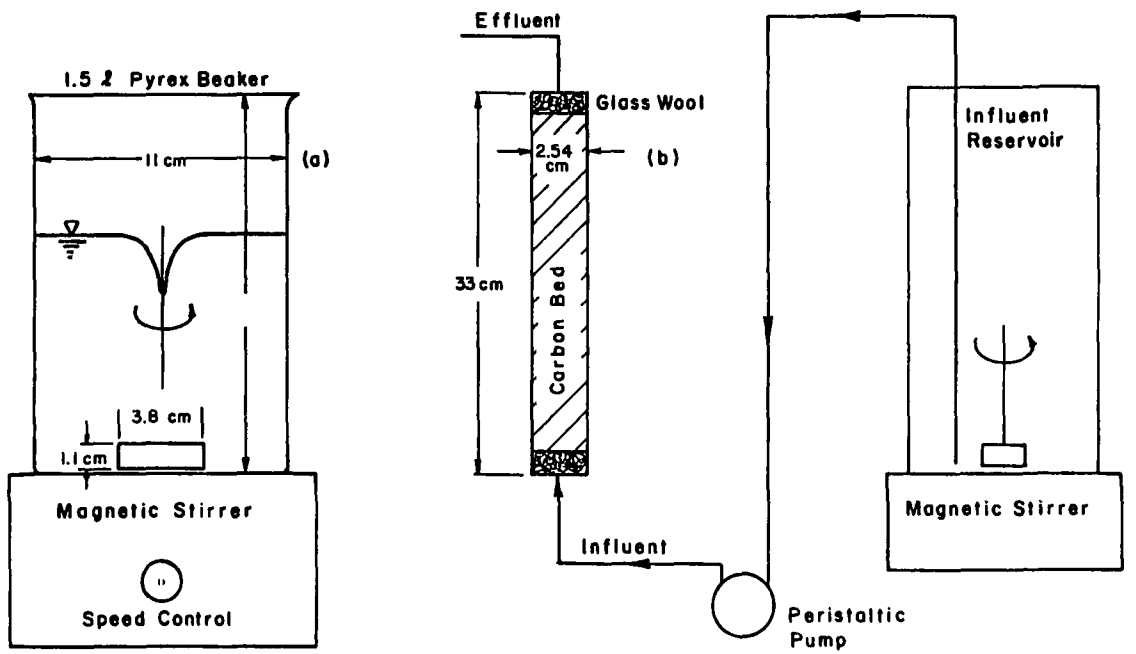

Figure 1. Experimental Apparatus: a. batch reactor; b. packed column experiments.

SECTION 5

EXPERIMENTAL PROCEDURE

BATCH MODE EXPERIMENTS

All experiments were conducted with batch reactors (1500 mℓ pyrex beakers) containing one liter of Cr(VI) solution prepared from a stock 10^{-2} M Na_2CrO_4 solution. The range of Cr(VI) concentrations was 5 x 10^{-5} M to 5 x 10^{-3} M (2.6 to 260 ppm) and the ionic strength was 10^{-1} M NaCl. The initial pH values were adjusted with 0.1 M HCl or NaOH solution and recorded with a pH-meter (Beckman, pHasar-I) equipped with a combination electrode (Beckman, Cat. No. 37501). The beakers were well mixed by a magnetic stirrer and the stirring speed was monitored with a strobotac (General Radio, Type 1531). At the end of predetermined intervals, 10 mℓ of samples was pipetted from the reactor and centrifuged at 15,000 g for 10 minutes with a centrifuge (International Model HT) to separate the residual carbon particles from solution prior to chromium analysis.

Torque on the stirring magnet to determine power input to the vessels was monitored with a Motomatic-Motor-Generator controlled speed system (Electro-Craft Corp. Model No. E-650-M).

PACKED COLUMN EXPERIMENTS

All experiments were conducted in stainless steel or plexiglass columns, having an inside diameter of one inch. The amount of carbon used was determined by mass and was placed loosely in columns with glass wool to insure even distribution of flow at both ends. All solutions were prepared the same as in the batch mode. Variable speed peristaltic pumps (Cole-Parmer Masterflex) were used to maintain a consistant flow rate throughout the experiments and avoid contamination in the pump head. Samples were collected in 100 mℓ bottles at predetermined time intervals and covered prior to chromium analysis.

The experimental apparatus configurations are shown in Figure 1 for batch and packed column reactors.

Regeneration of Exhausted Carbon

Adsorption-Desorption Cycles--

The experimental parameters and procedure for each adsorption cycle were: Cr(VI) = 127.8 mg/ℓ, pH = 2.0, carbon dose = 10 g/ℓ, adsorption period = 1 hour, and total sample volume = 500 mℓ. At the end of the

reaction period the treated solution was replaced by another 500 mℓ of the same chromium solution while the carbon particles remained in the bottle. Two procedures were carried out for the study of the regeneration process. In the first procedure, carbon particles were regenerated only after nine consecutive adsorption cycles. In the second procedure, regenerations were made three times after every four consecutive cycles of adsorption. No compensation for the loss of carbon was made.

Caustic Regeneration--

In the caustic desorption method, chromium attached on the carbon surface was desorbed with 250 mℓ of NaOH with concentrations ranging from 0.25% to 20%. The reaction period was 16 hours. After this desorption period, the particles were rinsed twice (for five minutes each) with 100 mℓ distilled water.

Thermal Regeneration--

In the thermal activation method, the chromium-laden carbon particles were first dried in an oven at 103°C for 24 hours. The dried particles were then heated at an elevated temperature for reactivation. Application of a muffle furnace at a maximum temperature of 550°C was first tried. The result showed only partial recovery of the adsorption capacity. However, by employing a specially designed heating device at 950°C, a distinct improvement in the recovery of the adsorption capacity was observed. This device was finally used for the rest of the thermal regeneration study.

A steady flow of carbon dioxide (about 30 mℓ/min) was passed through the holding tube during the 30 minute heating period. The carbon particles were cooled in air at room temperature (23 ± 1°C) for 24 hours.

Combined Caustic-Thermal Regeneration--

In the combined caustic-thermal process, the chromium-laden carbon was first regenerated by caustic desorption (1% NaOH), and then the carbon particles were dried at 103°C and thermal activated at 950°C in CO_2 gas as mentioned above.

Desorption Capacity--

Carbon was exhausted in a packed column, 10 grams carbon, by treating approximately 16 liters of 1×10^{-3} M Cr(VI) or 52 ppm. The effluent was saved and the amount of chromium on the carbon surface was determined by analysis of the effluent. The carbon was then regenerated by a caustic or acid solution to determine the maximum desorptive capacity of each solution and the desorptive cycle was repeated if all of the Cr(VI) was not removed.

Chromium Analysis--

The residual Cr(VI) concentrations were determined by the purple (540 nm) s-diphenyl carbizide-chromate complex with a UV-visible spectrophotometer (Hitachi-Perkin Elmer). The Cr(III) concentrations were determined by, first oxidizing the samples with potassium permanganate, then determining the total chromium as Cr(VI) and obtaining the Cr(III) concentration by subtracting the Cr(VI) from the total. Detailed analytical procedures were described in Standard Methods,(26) except that boiling-oxidation time was

extended from a recommended 3 minutes to 10 minutes with glass beads to assure total oxidation. This modification was found necessary because there were occasions when Cr(II) appeared in solution as results of further Cr(III) reduction by activated carbon.

SECTION 6

RESULTS AND DISCUSSION

ACTIVATED CARBON-SELECTION, PHYSICAL AND CHEMICAL PROPERTIES

The activated carbon selected for this study was Filtrasorb 400, provided by Calgon Co., Pittsburgh, Pennsylvania. The selection of this carbon was based on the available physical and chemical data for the carbon, as well as the potential of this particular carbon for chromium removal.

Filtrasorb 400 is a granular activated carbon having a relatively large surface area and high resistance to abrasion. Table 1 lists the various physical properties of the carbon, according to the manufacturer and our laboratory.

Filtrasorb 400 is apparently an H-type activated carbon according to the classification of Steenburg (27). An H-type carbon is characteristic of activated carbons produced under anoxic conditions at high temperatures, greater than 900°C, and which in contact with water raise the pH of solution through hydrolytic reactions and adsorb only acids (28). The effects of Filtrasorb 400 on blank solutions containing 0.1 M NaCl for ionic strength for both batch and packed column are exhibited in Figure 2 (a, b and c).

As shown, the pH of solution always increases upon contact with Filtrasorb 400. In the batch reaction vessels the magnitude of increase is proportional to the carbon dose, while the pH increases to about 10 and gradually decreases, approaching equilibrium at the influent pH after successive bed volumes of the influent pass through a column.

The electrokinetic surface charge characteristics of Filtrasorb 400 in comparison to a variety of other commercial carbons is shown in Figure 3 (15). The electrophoretic mobilities of the carbons are shown as functions of pH. The pH at which zero electrophoretic mobility occurs is known as the pH of zero point of charge, pH_{zpc} (29). High pH_{zpc} is typical for H-type carbons. The pH_{zpc} for Filtrasorb 400 compared to other carbons tested may partially explain the increased affinity of Filtrasorb 400 toward anionic species in solution, such as Cr(VI) (15).

Filtrasorb 400 has been proven effective for Cr(VI) removal by previous investigators. Huang and Wu,(24) along with Kim and Zolteck,(25) obtained good Cr(VI) removal efficiencies with Filtrasorb 400 activated carbon.

TABLE 1. PHYSICAL PROPERTIES AND SPECIFICATIONS OF ACTIVATED CARBON, CALGON FILTRASORB 400*

Physical Properties		
Total surface area, m^2/g (N_2, BET method)	1050 - 1200	(941†)
Bulk density, lbs/ft^3	25	
Partical density wetted in water, g/cc	1.3 - 1.4	
Pore volume, cc/g	0.94	
Effective size, mm	0.55 - 0.165	
Uniformity coefficient	1.9 or less	

Specifications	Specifications	Typical Analysis
U.S. Standard Series Sieve Size		
Larger than No. 12	Max. 5%	3%
Smaller than No. 40	Max. 5%	1%
Mean particle diameter, mm	0.9 - 1.1	1.0
Iodine number, minimum	1050	1100
Abrasion number, minimum	75	80
Moisture	Max. 2.0%	0.5%
Ash content	8%†	

*Information was provided by the manufacturer unless otherwise indicated.

†Determined in our laboratory.

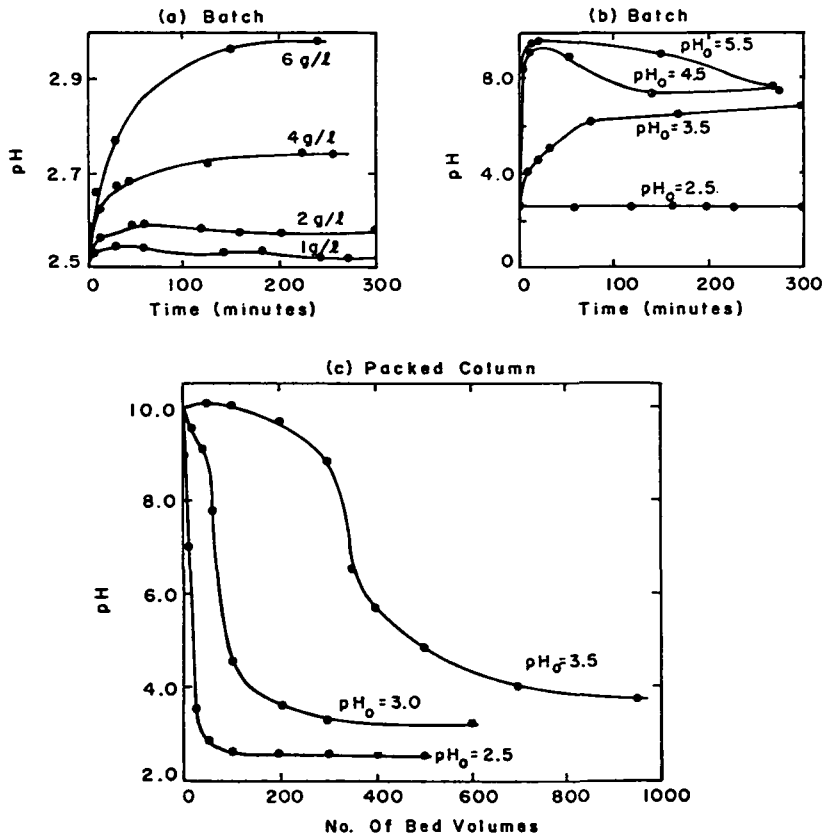

Figure 2. The effect of Filtrasorb 400 on solution pH:

a. in batch reactor with a given initial pH = 2.5 and varying carbon dosages.

b. in batch reactor with a given carbon dose = 2 g/ℓ and varying initial pH.

c. in packed columns with varying initial pH in the influent.

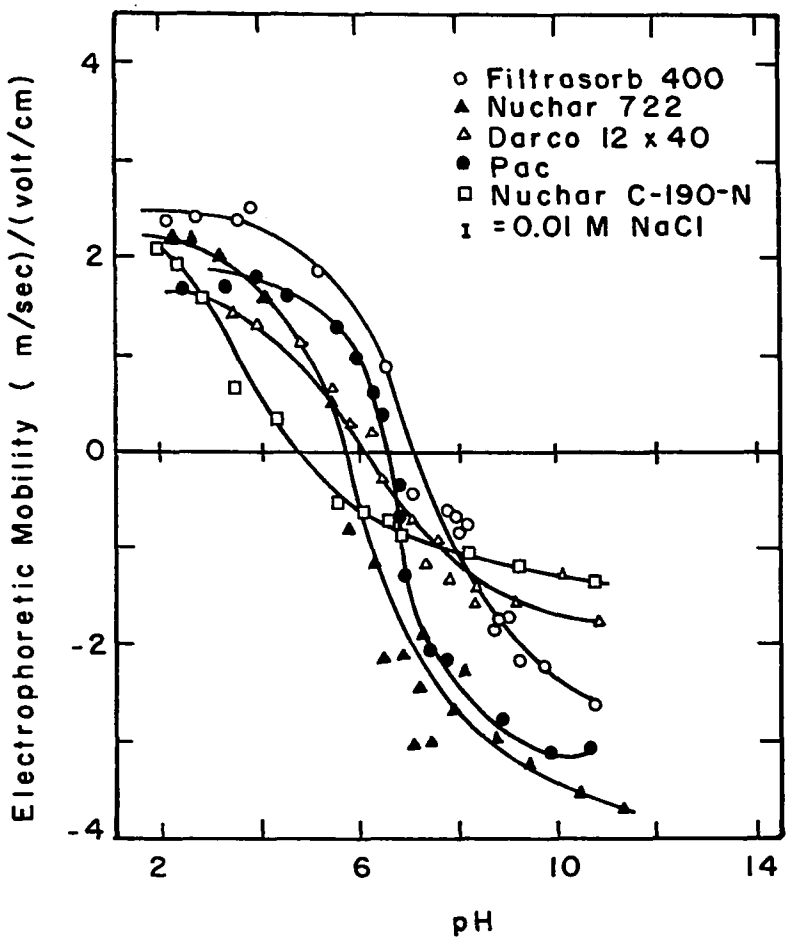

Figure 3. The electrophoretic mobility of various commercial activated carbons (after Huang and Ostovic) (15).

Cr(VI) Removal from Solution

The removal of Cr(VI) from solution occurs through several steps of interfacial reactions: 1) the direct adsorption of Cr(VI) onto the carbon surface; 2) the reduction of Cr(VI) species to Cr(III) by carbon on the surface; and 3) adsorption of the Cr(III) species produced, which occurs to a much lesser extent than the adsorption of the Cr(VI) species. The rate of each reaction depends on the following mechanisms: a) the transport of Cr(VI) anions, $HCrO_4^-$, by molecular or eddy diffusion, toward the carbon surface; b) chemical reactions, reduction and/or adsorption, which take place on the external carbon surface; c) desorption and back transport of the Cr(VI) and Cr(III) species from the external surface into the bulk phase; d) inner transport of the Cr(VI) and Cr(III) species into the internal surfaces bounding the micropores and capillaries of the carbon; e) chemical reactions, reduction and/or adsorption, taking place at the internal

surfaces; and f) back transport of the Cr(VI) and Cr(III) species across the internal surface and the external interface into the bulk phase. Figure 4 shows schematically the interactions of the most common Cr(VI) and Cr(III) species with the external and internal carbon surfaces which are indicated by the appropriate numbers and letters on the figure.

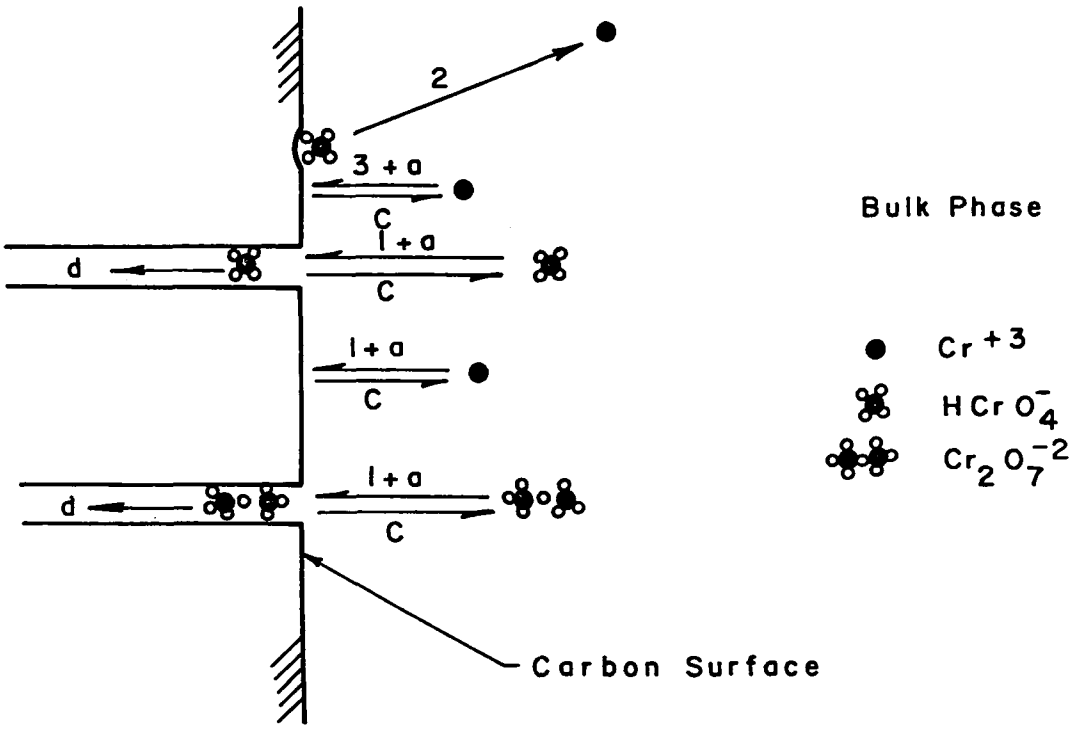

Figure 4. A simplified view of the chemical and physical interactions of chromium with activated carbon in dilute acidic medium.

Reduction Reaction at the Surface--

Hexavalent chromium species are powerful oxidizing agents. The reduction potentials for the various Cr(VI) species, in aqueous solution, compared to other common oxidants, are shown in Figure 5, calculated from Latimer (30).

It should be noted that $HCrO_4^-$ is the most predominant species for dilute acidic solutions, (Appendix A) and is not only a stronger oxidizing agent, but also has a much lower activation energy than the $Cr_2O_7^{-2}$ species, which is a slow acting oxidant even in 1 M H^+ solution (30). It is the $HCrO_4^-$ species which is the most active and takes part in the surface reduction reaction.

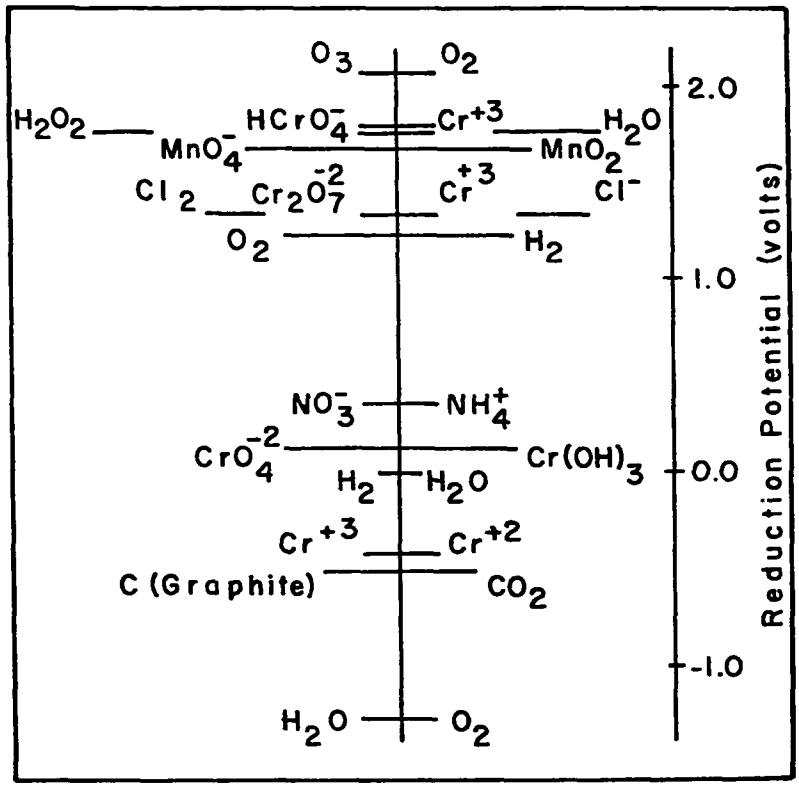

Figure 5. Reduction potentials of several common oxidizing agents (after Latimer) (30).

Surface Reaction Kinetics--

Normally, reactions which occur on surfaces, such as granular carbon particles, do not follow simple reaction order kinetics, due to the finite number of surface sites available for the reaction to occur. Therefore, the reduction rate, $\frac{dCr(VI)}{dt}$ or $\bar{v}_{red}$, will reach a maximum reaction velocity, V_{max}, as the concentration of the reactant, Cr(VI)(mole-ℓ^{-1}), increases or the reaction rate will become zero order as the concentration of Cr(VI) becomes sufficiently large (31,32). The expected results for this type of reaction are shown in Figure 6, where the ordinate is quantity $\bar{v}_{red}/v_{max}$ and the abiscissa represents the increasing reactant or Cr(VI) concentration as $HCrO_4^-$.

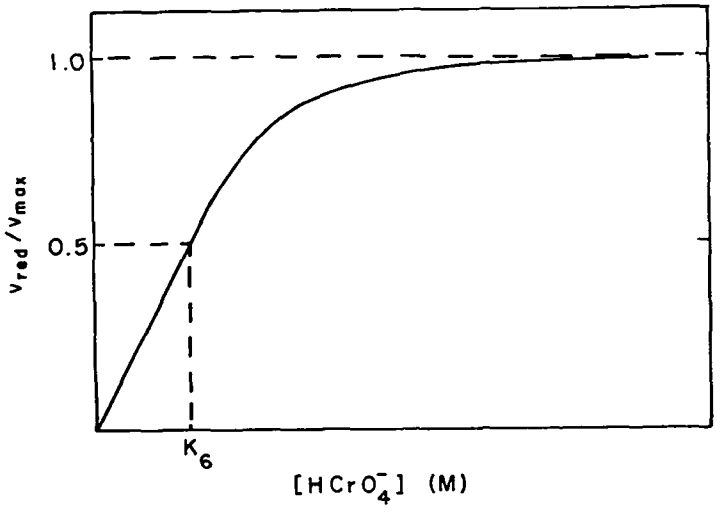

Figure 6. Ratio of observed reduction rate to the maximum rate as a function of $HCrO_4^-$ Cr(VI) concentration.

The quantity K_6 shown in Figure 6 represents the concentration of Cr(VI) at which v_{red} is equal to one half of v_{max}. This reaction is similar to first order Michaelis-Menten enzyme reactions, where the reaction rate is limited by the number of active reaction sites available or the carbon dose, C, in this case.

It was noted that both adsorption and reduction reactions occurred simultaneously. The reduction reaction may be obtained by considering the following stoichiometry of the reaction:

$$HCrO_4^- + 7\ H^+ + 3e \rightleftarrows Cr^{+3} + 4\ H_2O \qquad (1)$$

This implies that the rate of Cr(VI) removal due to reduction must also equal the rate of production of Cr(III). Therefore the rate of reduction may be written as:

$$v_{red} = \frac{dCr(III)}{dt} = -\frac{dCr(VI)}{dt}_{red} = \frac{v_{max}\,[HCrO_4^-][C]}{K_6 + [Cr(VI)]} \qquad (2)$$

where v_{red} = rate of Cr(VI) reduction (mole-ℓ^{-1}-min^{-1})

v_{max} = maximum rate of Cr(VI) reduction per unit mass of carbon (mole-g^{-1}-min^{-1})

$[HCrO_4^-]$ = concentration of bichromate in solution (mole-ℓ^{-1})

[C] = mass of carbon applied per unit volume ($g\text{-}\ell^{-1}$)

[CrVI] = concentration of total hexavalent chromium in solution ($mole\text{-}\ell^{-1}$)

K_6 = Cr(VI) concentration at which the rate of reduction equals one half of v_{max} ($mole\text{-}\ell^{-1}$)

Figure 7 shows typical batch reaction data for the removal of Cr(VI) (Figure 7a) and production of Cr(III) (Figure 7b). The rate of reduction at any time may be determined by the instantaneous slope of a line struck tangent to the Cr(III) production curve. By taking the slope at t = 0, the initial conditions are all known. Therefore, knowing that $[HCrO_4^-] = \alpha_1 \times [Cr(VI)]$, where α_1 is the fraction of the total Cr(VI) species in the $HCrO_4^-$ form and when Cr(VI) < 1×10^{-3} M, then $\alpha_1 \simeq 1.0$ (Appendix A), Equation (2) can be inverted to yield:

$$\frac{1}{v_{red}} = \frac{K_6}{v_{max}[C]} \times \frac{1}{[Cr(VI)]} + \frac{1}{v_{max}[C]} \tag{3a}$$

Therefore, plotting 1 ÷ initial v_{red} vs 1 ÷ initial [Cr(VI)] results in a linear plot having an intercept = 1 ÷ $\{v_{max}[C]\}$ and a slope = K_6 $\{v_{max}[C]\}$ as shown in Figure 8. Since the initial conditions are known, pH = 2.50, [C] = 2 g/ℓ, and a constant mixing intensity, the reduction rate equation may now be evaluated from the results in Figure 7 and 8 as:

$$\frac{dCr(III)}{dt} = -\left(\frac{dCr(VI)}{dt}\right)_{red} = \frac{1.0 \times 10^{-5}\,[HCrO_4^-][C]}{2.4 \times 10^{-4} + [Cr(VI)]} \tag{3b}$$

The rate of the reduction reaction is also influenced by the rate of mass transport or mixing intensity in the system, the pH in the bulk solution, and the amount of Cr(III) which has been produced and is present in the bulk solution.

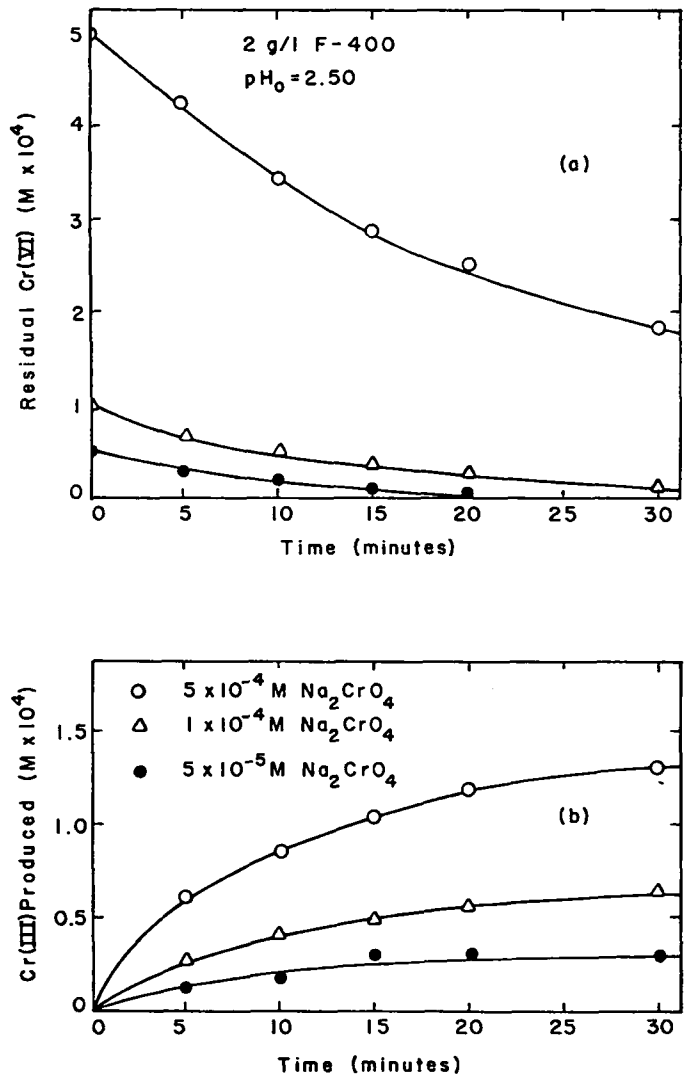

Figure 7. a) Batch removal of Cr(VI) and

b) production of Cr(III).

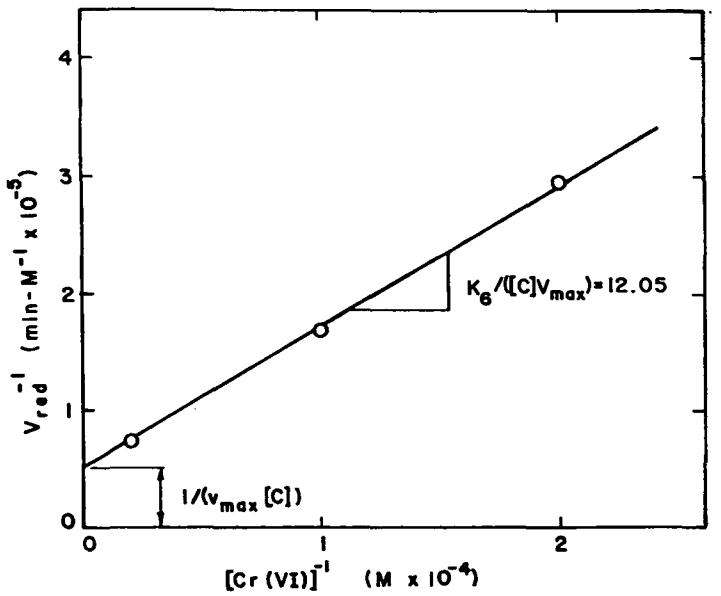

Figure 8. Inverse plot of initial reduction rate and Cr(VI) concentration (data were taken from Figure 7).

Effect of Mixing Intensity on Cr(VI) Reduction

The rate of mass transport, or mixing in the reaction vessel, effects the rate of Cr(VI) reduction and therefore becomes the rate limiting step at low levels of mixing in the system. Figure 9 shows the removal of Cr(VI) and the corresponding production of Cr(III) at increasing mixing intensities, i.e., angular velocity of the magnetic stirring bar, $\omega(sec^{-1})$.

The mass transport in a mixed vessel is a function of the velocity gradient in the system, which can be determined by the power input to the vessel through the stirring bar or paddle. By measuring the torque on the stirring motor at known values of ω, the power input to the reaction vessel can be determined by:

$$P = T \times \omega \tag{4}$$

where P = power input to the system (in-lb/sec)

T = torque applied to the mixing shaft (in-lb)

ω = angular velocity of the mixing shaft (sec^{-1})

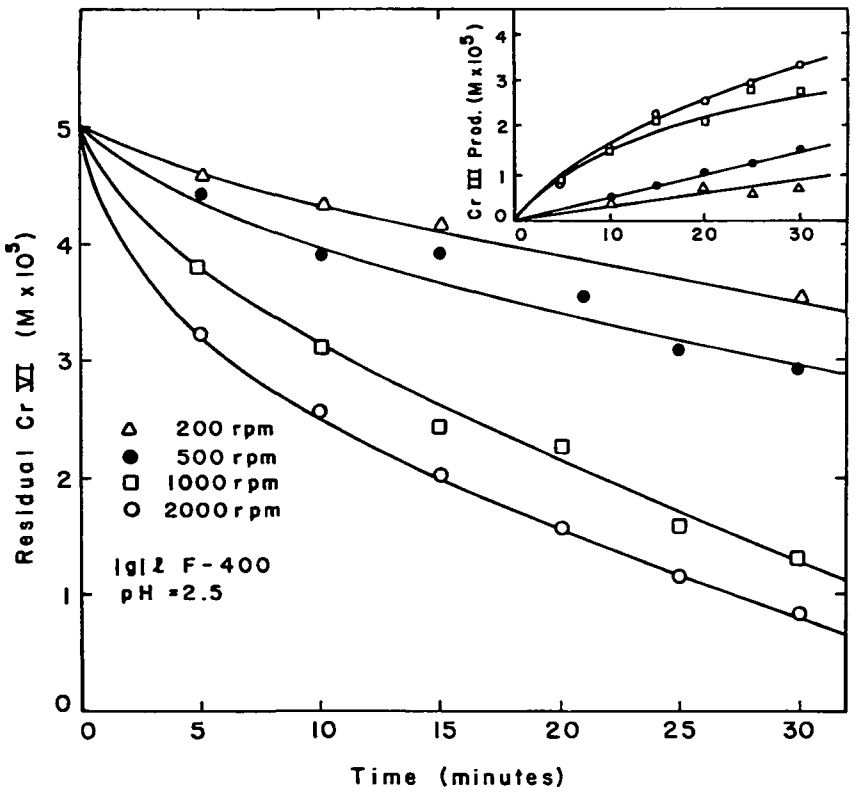

Figure 9. The removal of Cr(VI) and production of Cr(III) at different mixing intensities.

and the mean velocity gradient, G (sec^{-1}) under turbulent conditions may then be estimated by the Saffman-Turner equation:

$$G = \{\frac{2P}{15\pi V\mu}\}^{\frac{1}{2}} \tag{5}$$

where V = the volume of the reaction vessel (in^3)

μ = the dynamic viscosity of the bulk solution ($lb\text{-}sec/in^2$)

A summary of these results for various mixing speeds and 1-liter of 0.1 M NaCl solution are shown in Table 2.

TABLE 2. CALCULATED VALUES FOR POWER INPUT AND MEAN VELOCITY GRADIENTS IN A 1 LITER REACTION VESSEL AND A STANDARD 1 INCH STIRRING BAR

ω ($sec^{-1} \times 10^{-1}$)	T measured (in-lb)	P (in-lb/sec $\times 10^{-2}$)	G (sec^{-1})
0.17	0.01	0.06	1.69
0.33	0.01	0.12	2.39
0.83	0.02	0.60	5.35
1.67	0.03	1.80	9.27
2.50	0.04	3.20	13.10
3.33	0.05	6.00	16.90

The mass transfer rate in solution will effect the half-velocity constant, K_6, in equation 3, while v_{max} will remain unchanged. Therefore, K_6 may be calculated from the initial rates of Cr(III) production in Figure 8, and the effect of G on K_6 under these conditions is shown in Figure 10. The slope of the log-log plot for K_6 versus G indicates that K_6 is a function of G, or

$$K_6 \simeq \frac{2.7 \times 10^{-3}}{G} \tag{6}$$

Effect of Cr(III) on Reduction

The production of Cr(III) at the carbon surface results in an accumulation of Cr(III) in the bulk solution and a decline in the Cr(III) concentration gradient between the surface and bulk phases. This results in a decreased driving force to remove the Cr(III) from the surface and subsequently the surface sites are tied up longer by the Cr(III) produced. Therefore, increasing Cr(III) concentration in the bulk solution will competitively inhibit the reduction reaction and the rate of reduction will be decreased or:

$$\frac{dCr(III)}{dt} = -\left(\frac{dCr(VI)}{dt}\right)_{red} = \frac{v_{max}[HCrO_4^-][C]\ K_3}{K_3K_6 + K_6[Cr(III)] + K_3[Cr(VI)]} \tag{7}$$

where K_3 = the constant of trivalent inhibition (mole-ℓ^{-1})

and [Cr(III)] = the concentration of Cr(III) in the bulk phase (mole-ℓ^{-1}).

The rate of reaction at any Cr(III) concentration may be taken from the slope of the line tangent to that point on the Cr(III) production curve. Therefore, by striking tangents to points of equal Cr(III) concentrations, 5×10^{-5} and 2.5×10^{-5} M in Figure 7b, and knowing the Cr(VI) concentration in the bulk solution at that time, from Figure 7a, the inverse of equation 7 may be plotted as shown in Figure 11, where all of the lines intersect the ordinate at $1/v_{max}$ [C] and the slope of the line is:

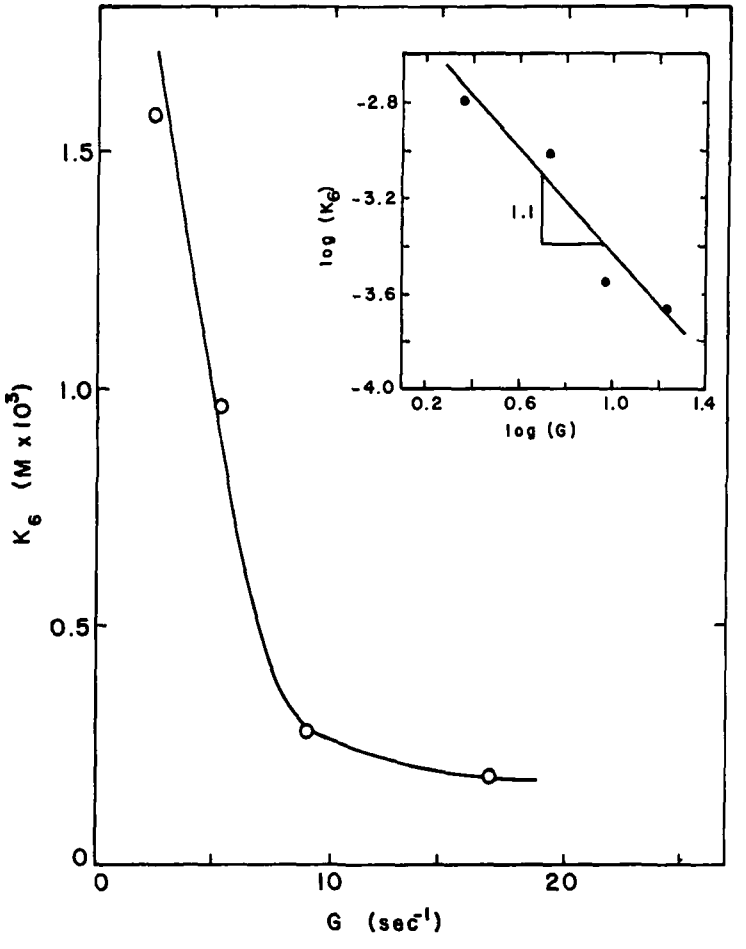

Figure 10. The effect of velocity gradient on the reduction rate constant (K_6).

$$\left(1 + \frac{[Cr(III)]}{K_3}\right) \frac{K_6}{v_{max}[C]} \tag{8}$$

where K_6, v_{max} and [C] are known values from Figure 8 (2.41×10^{-4} M, 1.0×10^{-5} moles-min^{-1}-g^{-1}, and 2.0 g/ℓ) and [Cr(III)] was constant at 5×10^{-5} and 2.5×10^{-5} M (2.6 and 1.3 ppm). K_3 can be evaluated from equation 8 and the slope of the lines in Figure 11. The values of K_3 are listed in Table 3. The average value of K_3 was 2.4 M x 10^{-5} M which was used for all subsequent calculations.

TABLE 3. REDUCTION REACTION VELOCITIES AND INHIBITION CONSTANTS WITH Cr(III) IN THE BULK SOLUTION

[Cr(III)] (M x 10^5)	Slope of v^{-1} vs $[Cr(VI)]^{-1}$ (min x 10^{-1})	K_3* (M x 10^5)
0	1.21	-
2.5	1.37	2.49
5.0	2.52	2.37
		$\bar{K}_3$ = 2.43 x 10^{-5}

* Calculated from equation 8.

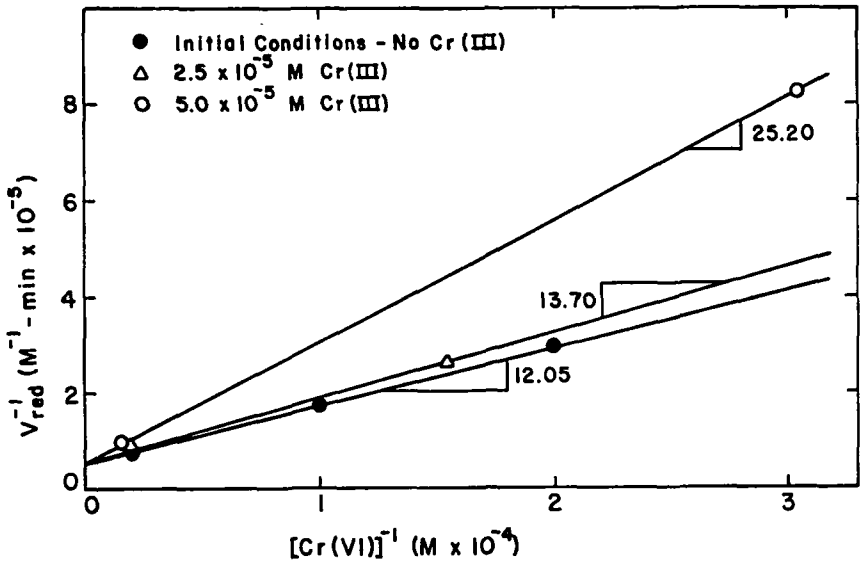

Figure 11. Inhibition of the surface reduction reaction due to Cr(III) in the bulk solution.

Effect of pH on Reduction

The reduction of Cr(VI) to Cr(III) involves the consumption of H^+ ions from solution, as shown by equation 1, for the reduction half reaction. A proposed overall reaction for Cr(VI) reduction at the carbon surface is:

$$4\ HCrO_4^- + 3\ C\ (\text{amorphous}) + 16\ H^+ \rightleftarrows 4\ Cr^{+3} + 3\ CO_2 + 10\ H_2O \qquad (9)$$

which implies the consumption of H^+ ions, per Cr(III) ions produced, occurs at a 4:1 ratio. Therefore, the H^+ concentration will limit the extent of Cr(III) produced and should strongly effect the rate of the reduction reaction.

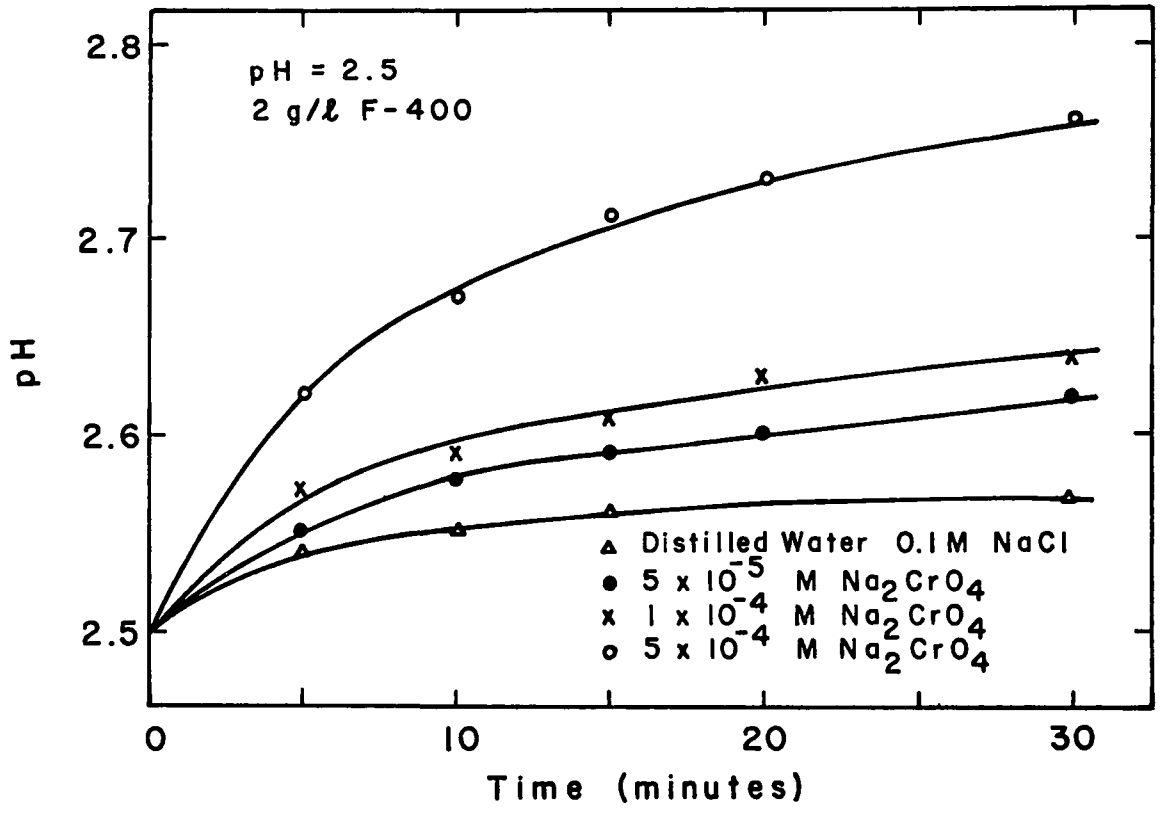

Figure 12. The increase in pH with increasing initial Cr(VI) concentration.

The change in pH of solution is shown in Figure 12 for increasing initial concentrations of Cr(VI), i.e., increasing magnitudes of Cr(III) produced, and compared to the change of pH for the carbon in solution without the presence of Cr(VI). As expected, the rate and magnitude of H^+ consumption increases proportionally with the amount of Cr(III) production.

Decreasing the H^+ concentration in solution effects the rate of reduction by increasing the concentration of Cr(VI) needed to reach the maximum reaction velocity, v_{max}. Therefore, the half velocity constant, K_6, will increase with decreasing H^+ concentration. The actual reaction rates at various pH's were determined by the instantaneous slope of the Cr(III) production curve shown previously in Figure 6b, at 5×10^{-4} M initial Cr(VI) concentration, 2 g/ℓ carbon dose, and having an initial pH of 2.5. The pH corresponding to each point in time was read from Figure 12, and the rate was corrected for the instantaneous concentration of Cr(III) in the bulk solution.

Therefore, K_6 may be expressed quantitatively by:

$$K_6 = \{(\frac{1}{v_{red}} - \frac{1}{v_{max}[C]}) \cdot [Cr(VI)] - 1\} \frac{K_3 \, v_{max} \, [C]}{[Cr(III)]} \tag{10}$$

and the values of K_6 are summarized in Table 4.

TABLE 4. A SUMMARY OF THE HALF SATURATION CONSTANT, K_6, AS THE pH IN SOLUTION INCREASES.

Time (min)	[Cr(VI)] (M x 10^4)	[Cr(III)] (M x 10^4)	pH	v_{red} (M-min$^-$ x 10^6)	K_6* (M x 10^4)
0	5.0	0	2.50	13.3	2.41
5	4.24	0.61	2.62	6.80	3.20
10	3.41	0.85	2.67	4.15	3.66
15	2.84	1.03	2.71	2.93	3.87
20	2.48	1.16	2.73	2.12	4.34
30	1.79	1.29	2.76	1.30	4.81

* Calculated from equation 10.

The results of K_6 versus pH are shown in Figure 13. From the figure, the reduction rate constant, K_6, exhibits an approximate 1st order dependence on $[H^+]$ in solution. Therefore, K_6 is written as:

$$K_6 \simeq 4.8 \times 10^{-6} \, G \, [H^+] \tag{11}$$

and the overall reduction rate equation becomes:

$$-(\frac{dCr(VI)}{dt})_{red} = \frac{2.4 \, [HCrO_4^-][C] \, G \, [H^+]}{1.2 + 4 \times 10^4 \, [Cr(III)] + 2.4 \times 10^5 \, G \, [H^+][Cr(VI)]} \tag{12}$$

ADSORPTION OF Cr(VI)

Equilibrium Adsorption Capacity

The adsorptive capacity of the carbon for Cr(VI) depends upon the ionic strength of the bulk solution (0.1 M NaCl for all experiments performed in this study), the pH of the bulk solution, and the concentration of Cr(VI) in the bulk solution at equilibrium.

Batch experiments were run to determine the equilibrium adsorptive capacity, Γ eq. (μm/g), as a function of bulk pH and Cr(VI) concentration. Typi-

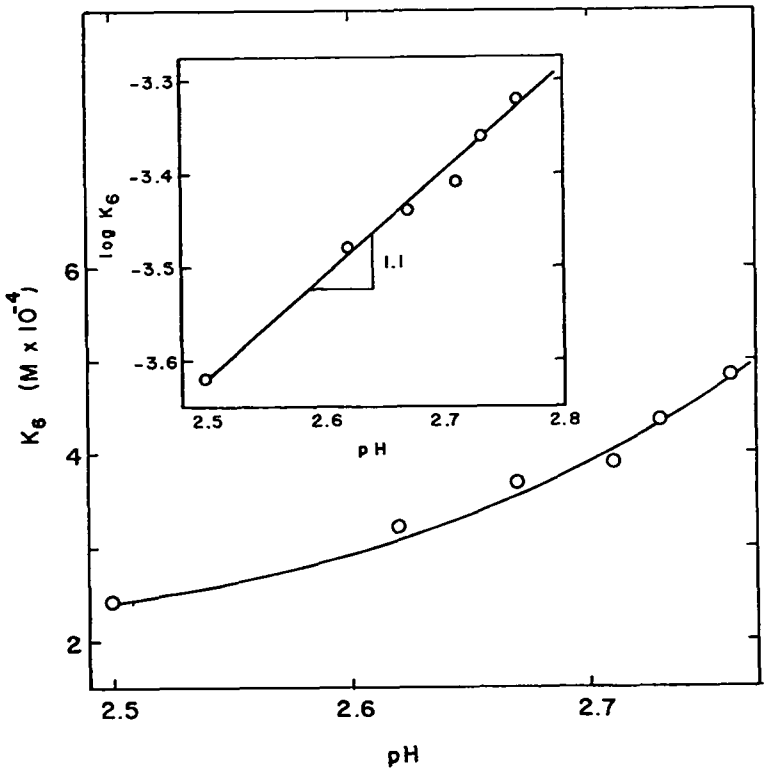

Figure 13. The effect of pH on the reduction rate constant.

cal batch results are shown in Figure 14 for an initial Cr(VI) concentration of 5 x 10^{-3} M and increasing initial pH values. Equilibrium is observed to occur at the end of 5 hours contact time. Initial and final pH's are indicated on the graph and little reduction of Cr(VI) was observed to occur due to elevated pH's observed (greater than 3.5 after 1 hour).

Adsorption of the Cr(VI) species due to the condensation of H_2CrO_4 within the carbon micropores, and the adsorption of each $HCrO_4^-$ molecule consumes one H^+ from solution. An adsorption equation can then be written as an equilibrium between H_2CrO_4, which accumulates in the porous phase, $[H_2CrO_4]_p$, the bulk proton concentration, $[H^+]_b$, and Cr(VI) in the bulk phase, $[HCrO_4^-]_b$, or:

$$H^+ + HCrO_4^- \rightleftarrows H_2CrO_4; \qquad K_e \tag{13a}$$

where

$$K_e = \frac{[H_2CrO_4]_p}{[H^+]_b\ [HCrO_4^-]_b} \tag{13b}$$

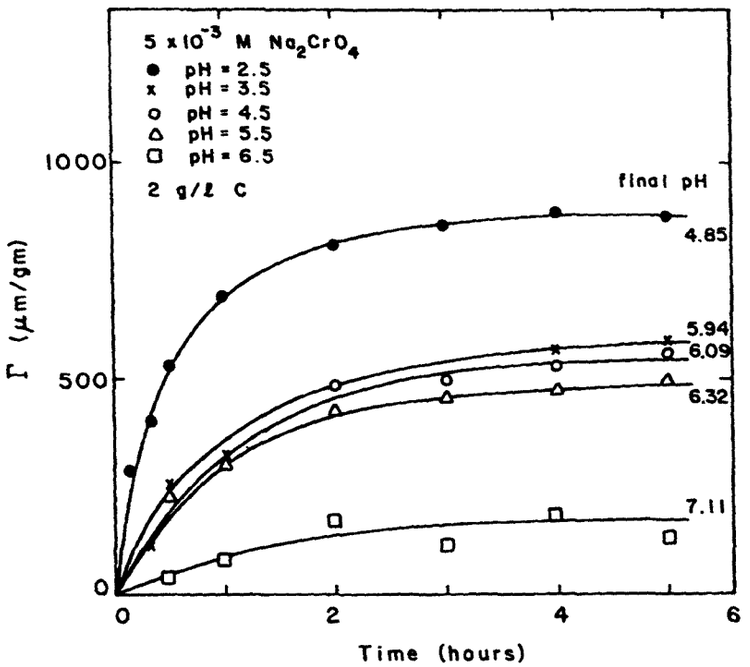

Figure 14. Cr(VI) adsorption density versus reaction time.

Values of K_e have been calculated from Figure 14 and the results are shown in Table 5.

The results of Table 5 show that K_e is not a constant, but is itself dependent upon pH and Cr(VI) concentration in the bulk phase. This result is expected, due to the effect of pH on the surface charge of the carbon which acts as an electrostatic driving force for adsorption of Cr(VI) species and due to the effect of the Cr(VI) concentration gradient as a driving force, along with the capillary forces involved in the carbon micropores.

An empirical equation for K_e may be derived by assuming K_e will have the same order dependence on pH regardless of Cr(VI) concentration, or that a plot of log K_e against pH will result in a straight line with an intercept, b, which will decrease as the concentration of Cr(VI) is decreased. Figure 15 shows the results of such an analysis of the data from Table 5. The adsorption constant K_e can be expressed as:

$$\log K_e = 0.8\ pH + b \qquad (14a)$$

where

$$\log b = \frac{-1}{20} \log [Cr(VI)]_b + 0.41 \qquad (14b)$$

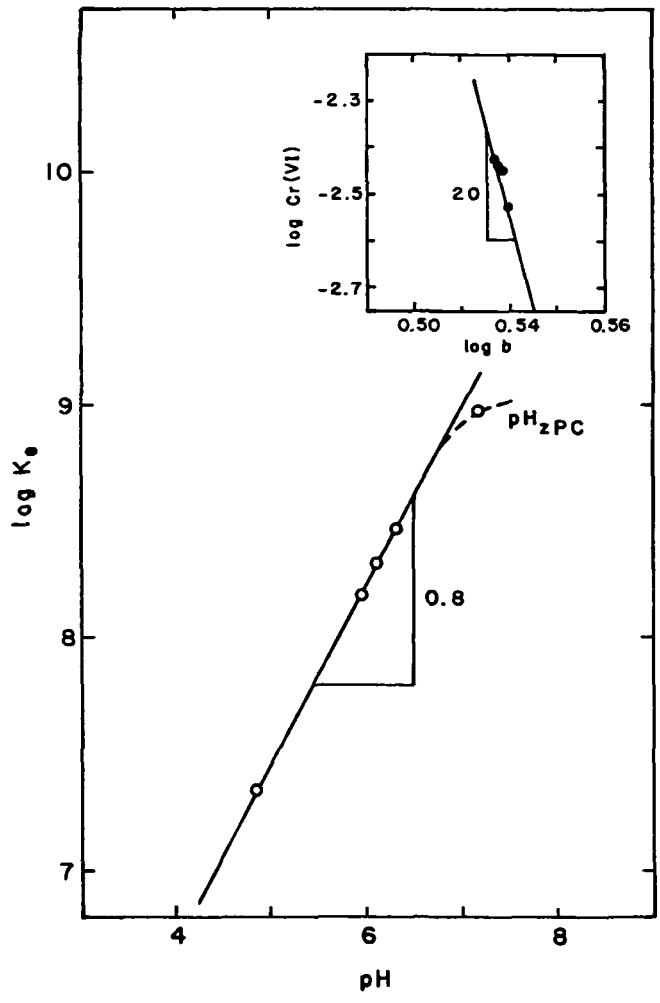

Figure 15. Adsorptive equilibrium constant as a function of pH and Cr(VI) concentration in the bulk phase.

It should be noted, however, that these equations are strictly empirical and have no theoretical basis for their prediction. Equations 14a and 14b are accurate for a pH range of 2.5 to 7.0, since higher values would be above the pH_{zpc} and would not be expected to conform. The lower pH values would in-

TABLE 5. EQUILIBRIUM CONSTANTS FOR FORMATION OF H_2CrO_4 IN THE CARBON MICROPORES.

pH_o*	pH_e†	[C] (g/ℓ)	Γ_e (μm/g)	$[H_2CrO_4]_p$‡ (M)	[Cr(VI)] (M x 10^3)	K_e§ (M^{-1} x 10^{-8})	log K_e
2.5	4.85	2.0	870	0.93	3.02	0.22	7.34
3.5	5.94	2.0	590	0.63	3.62	1.51	8.18
4.5	6.09	2.0	560	0.60	3.56	2.06	8.31
5.5	6.32	2.0	495	0.53	3.75	2.96	8.47
6.5	7.15	2.0	180	0.27	4.28	8.78	8.94

* Initial pH in bulk solution.

† pH in bulk solution at equilibrium.

‡ Calculated from Γ_e using an internal pore volume of 0.94 ml/g from Table 1.

§ Calculated from equation 13b.

crease the acidity inside the micropores to the extent that reduction would occur faster than H_2CrO_4 condensation and all of the Cr(VI) would be reduced to Cr(III) and released back into solution.

A comparison of observed capacities and calculated capacities are shown in Table 6. The results show good agreement between actual and predicted values. The calculated values are shown to be slightly conservative, which would be desirable for actual system design.

Kinetics of Cr(VI) Adsorption

The transfer of Cr(VI) from the bulk solution into the surface pores of the activated carbon is driven by the charge forces between the carbon particles and the Cr(VI) species, the capillary forces which exist between the carbon micropores and the bulk solution, and the concentration gradient which exists across the surface-bulk interface. According to Weber and Morris (33), the rate of steady state transfer across this interface, $(dCr(VI)/dt)_{ads}$, will equal the driving force divided by the resistance, or:

$$-\left(\frac{dCr(VI)}{dt}\right)_{ads} = k\, a_c\, [C]\, \Delta\, Cr(VI) \qquad (15)$$

where k = transfer coefficient (ℓ-min^{-1})

a_c = effective transfer coefficient per unit mass of carbon (g^{-1})

TABLE 6. COMPARISON OF CALCULATED Γ_e VERSUS OBSERVED Γ_e

$[CrVI]_o$ (M) (x 10^3)	$[CrVI]_e$ (M) (x 10^3)	pH_o	pH_e	[C] g/ℓ	Γ_e observed (μm/g)	Γ_e predicted (μm/g)	Error (μm/g)	% Error
5.0	3.02	2.50	4.85	2.0	870	830	-40	-4.8
5.0	3.62	3.50	5.94	2.0	590	560	-30	-5.4
5.0	3.56	4.50	6.09	2.0	560	518	-42	-8.1
5.0	3.75	5.50	6.32	2.0	495	481	-14	-2.9
5.0	2.17	2.50	5.83	4.0	688	632	-55	-8.1
5.0	2.98	3.50	6.50	4.0	495	385	-110	-28.6
5.0	3.08	4.50	6.54	4.0	475	385	-90	-18.9
5.0	3.29	5.50	6.78	4.0	363	359	-4	-1.1
5.0	1.92	2.50	6.45	6.0	508	302	-206	-40.6
5.0	2.77	3.50	7.00	6.0	355	292	-63	-17.7
5.0	1.96	2.50	6.83	8.0	378	257	-120	-31.7
1.0	1.0 *	2.50	2.61		1280	1267	-13	-1.0
1.0	1.0 *	2.75	2.86		1130	1129	-1	-0.0
1.0	1.0 *	3.00	3.27		1070	935	-135	-12.6

* Data obtained from continuous flow packed column experiments run to equilibrium.

C = mass of carbon ($g\text{-}\ell^{-1}$)

Δ Cr(VI) = concentration difference across the surface bulk interface (M)

For the Cr(VI)-Filtrasorb system, the carbon inner-surface has an extremely high affinity for Cr(VI) and a concentration gradient will exist in favor of the bulk phase, and the driving force due to the concentration gradient will be:

$$\Delta \text{ Cr(VI)} = \{\text{Cr(VI)}_b - \pi \text{ Cr(VI)}_b\} \tag{16a}$$

where π is a partition factor between the surface and bulk phase Cr(VI) concentrations, or:

$$\pi = \frac{\Gamma}{\Gamma_e}$$

where Γ = amount of Cr(VI) adsorbed into the carbon (μ mole/g) μm/g

Γ_e = amount of Cr(VI) adsorbed into the carbon at equilibrium with the bulk concentration (μm/g)

From equation 15, the transfer coefficient, k, and the effective transfer per unit mass of carbon, a_c, may be lumped into a single constant, $k^*(\ell\text{-}g^{-1}\text{-}min^{-1})$, which will depend upon the pH of solution due to the change in the surface charge density and the subsequent effect on the electrokinetic driving force of Cr(VI) adsorption. Figure 16 shows the residual Cr_{total}, which is equal to the amount of total chromium remaining, Cr(VI) + Cr(III), as a result of Cr(VI) adsorption and is exclusive of Cr(VI) removal by reduction at constant initial conditions, except for increasing pH values. The slopes of lines tangent to the initial points yield the initial adsorption rate, $\{dCr(VI)_{ads}/dt\}_o$, when $\Gamma/\Gamma_e = 0$, which implies that:

$$\left(\frac{dCr(VI)}{dt}\right)_{ads} = k^* \, [H^+]^n \, [Cr(VI)] \, [C] \tag{17}$$

and the insert in Figure 16 shows the dependence of k* on the one-fifth power of $[H^+]$. A summary of the initial conditions in Figure 16 and the resulting values of k* are calculated in Table 7.

TABLE 7. EVALUATION OF k* AT KNOWN INITIAL CONDITIONS FOR pH, [C] AND [Cr(VI)].

[Cr(VI)] $(M \times 10^3)^o$	[C] (g/ℓ)	pH_o	$(\frac{dCr(VI)}{dt})_{ads}$ (M/min x 10^5)	$[H^+]^{1/5}$ (x 10)	k* calculated (ℓ-g^{-1}-min^{-1} x 10^2)
5.0	2.0	2.5	9.52	3.16	3.01
5.0	2.0	4.5	3.67	1.26	2.91
5.0	2.0	5.5	2.35	0.79	2.97
5.0	2.0	6.5	1.00	0.50	2.00†
					$\bar{k}^*$ = 2.93

† Excluded from average calculation due to the closeness of pH_{zpc}.

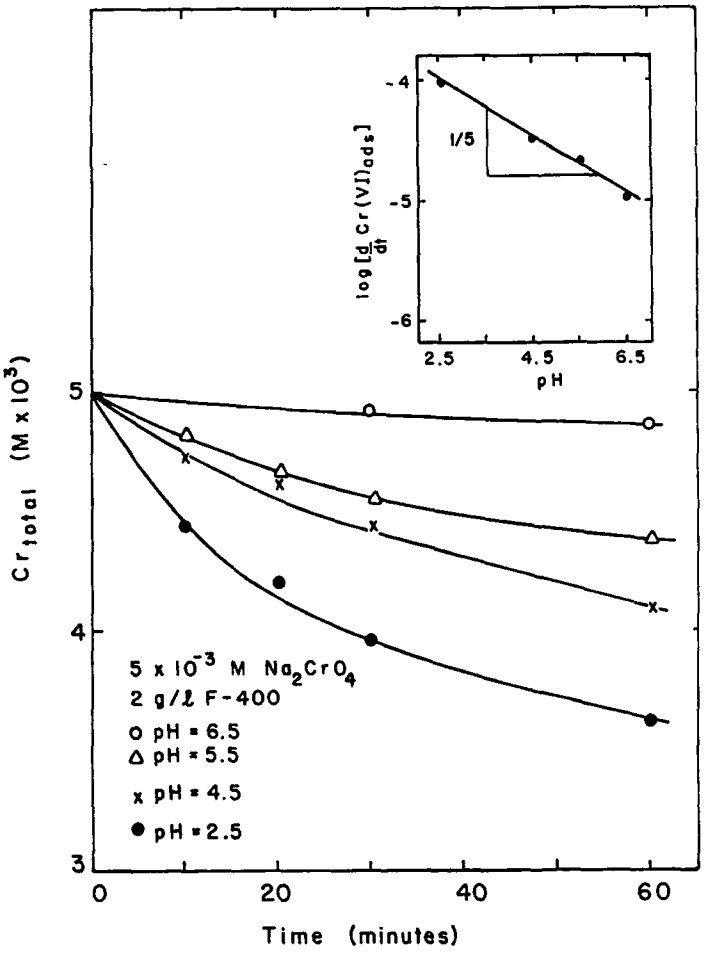

Figure 16. The removal of total chromium at various pH values in solution.

Therefore, the rate of Cr(VI) from solution may be written as:

$$\left(\frac{dCr(VI)}{dt}\right)_{ads} = -\ 2.9 \times 10^{-2}\ [H^+]^{0.2}[C]\ [Cr(VI)]\ \{1 - \frac{\Gamma}{\Gamma_e}\} \qquad (18)$$

where Γ_e may be calculated using equations 13 (b) and 14 (a and b).

The Effect of Mixing on the Adsorption of Cr(VI)

The reduction reaction at the carbon surface is controlled by the rate of mixing or velocity gradient in the reaction vessel. However, the adsorption of Cr(VI) species onto the carbon is controlled by the diffusion of the species into the micropores on the surface. Therefore, the mixing in solution would not be expected to influence the adsorption reaction as long as the rate of Cr(VI) transport to the surface is larger than the adsorption rate. Figure 17 showns the removal of Cr(VI) from solution at various stirring speeds.

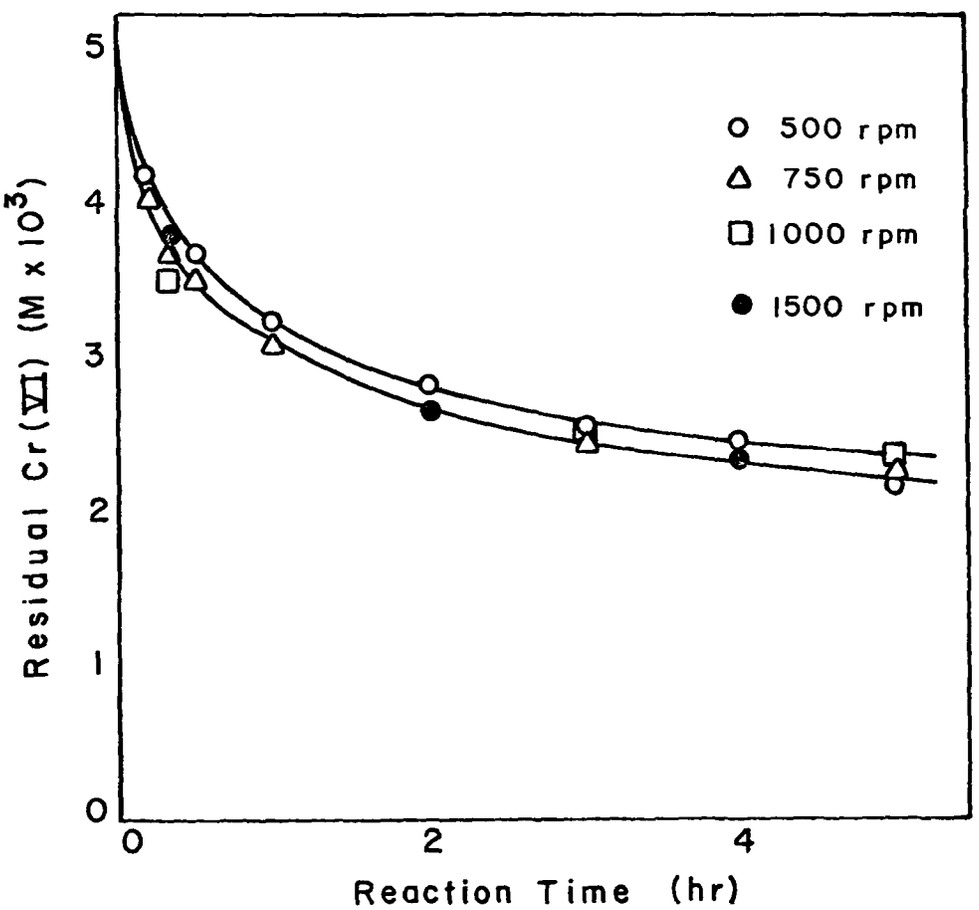

Figure 17. The removal of Cr(VI) at various stirring speeds; the effect on adsorption.

By using a much larger Cr(VI) concentration in these experiments, compared to the reduction experiments, 5×10^{-3} M vs 5×10^{-5} M, the reduction reaction velocity should be close to the maximum and mixing should effect adsorption rather than reduction. Therefore, as expected, Figure 17 shows little effect on Cr(VI) removal as long as the stirring speed in the reaction vessel is greater than 500 rpm ($G = 5.4\ sec^{-1}$), or G can be neglected in the rate equation for adsorption in a well-mixed vessel.

Packed Column Experiments

Loosely packed carbon columns were run to determine the importance of the various operational parameters in maintaining an efficient and effective system for removal of Cr(VI) and to minimize the amount of Cr(III) produced.

The duration time of these experiments was reported in number of bed volumes of influent passed through the column, where a single bed volume, v_b (ℓ), was the volume of the voids in the column. For Filtrasorb 400 packed loosely in one inch diameter columns, one bed volume was defined as:

$$V_b = \{1.26 \times 10^{-3}\ \ell/g\} \times M_c \qquad (19)$$

where M_c = mass of carbon in the column (g).

The effects of carbon bed depth, influent Cr(VI) concentration, and pH on the removal efficiency were studied in these experiments. Pre-washing of the carbon before contact with Cr(VI) was also investigated.

The influence of bed size on the removal efficiency is indicated in Figure 18 (a through d) for 10, 30, and 50 gram carbon beds, all receiving a constant influent of 2 gal/min/ft^2 or 44 mℓ/min, at pH 2.50, 10^{-3} M Na_2CrO_4 and 0.1 M NaCl. The inability of the carbon to remove all of the Cr(VI) over the first few bed volumes (Figure 18a) is due to the high initial pH observed, primarily due to the amount of H^+ ions needed to hydrolyze the carbon surface, as shown previously in Figure 2. Since there is no Cr(VI) present after 100 bed volumes for 30 or 50 gram carbon beds, the equality of the Cr(III) produced by the 30 and 50 gram carbon beds (Figure 18b) indicates that adsorption of the trivalent species does not occur and may be neglected.

The influent Cr(VI) concentration was varied from 1×10^{-4} M to 5×10^{-3} M Na_2CrO_4, 5.2 to 260 ppm as Cr, while the carbon bed size, influent pH, and flow rate remained constant, 50 g, 2.50, and 2 gal/min/ft^2, respectively. The results of these experiments are shown in Figure 19 (a through d). Figure 19 (a) shows a retardant effect of increased Cr(VI) concentration on the time required for the pH of the column to equilibrate as the surface hydrolysis reactions go to completion. This is due to the increased demand imposed on the H^+ concentration as the influent Cr(VI) concentration is increased and more Cr(III) is subsequently produced (Figure 19c) and more Cr(VI) is also adsorbed (Figure 19d).

The removal of Cr(VI) is incomplete for the initial bed volumes, (Figure 19 b) due to the high pH which is maintained for the first 100 bed volumes as a result of the H^+ demand for the hydrolysis reactions. The complete removal

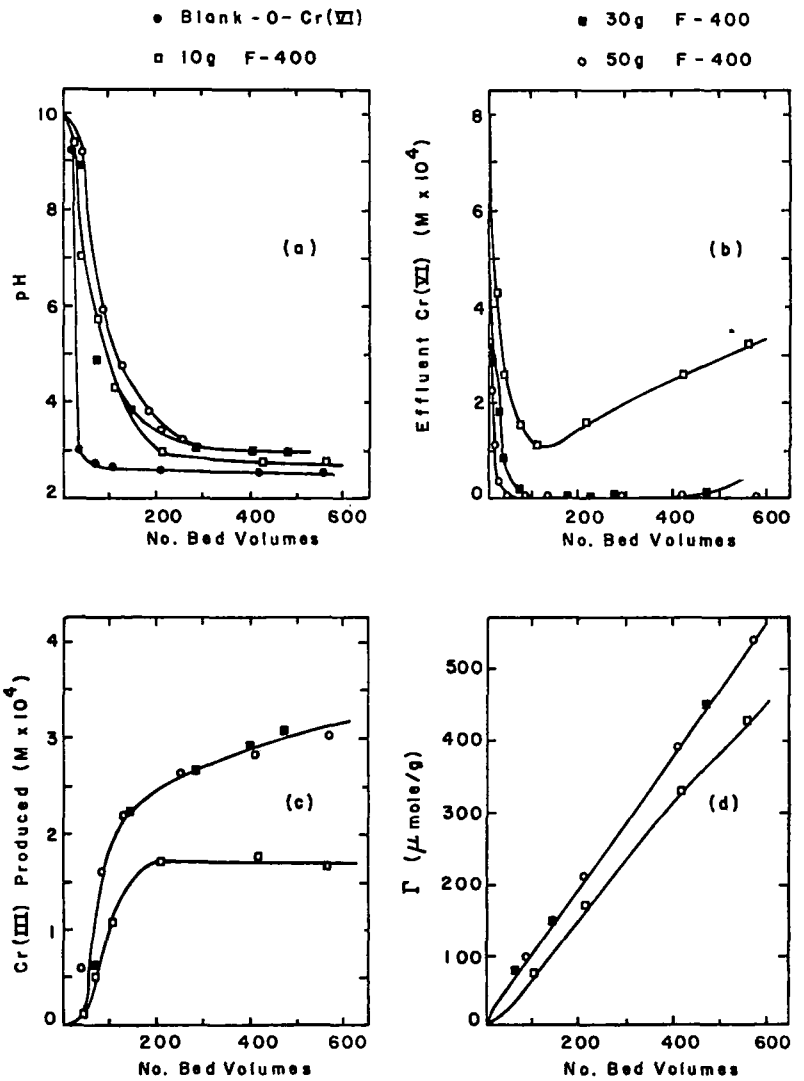

Figure 18. The effect of Carbon Bed size on:
a. pH
b. residual Cr(VI)
c. Cr(III) produced
d. the Cr(VI) adsorption density.

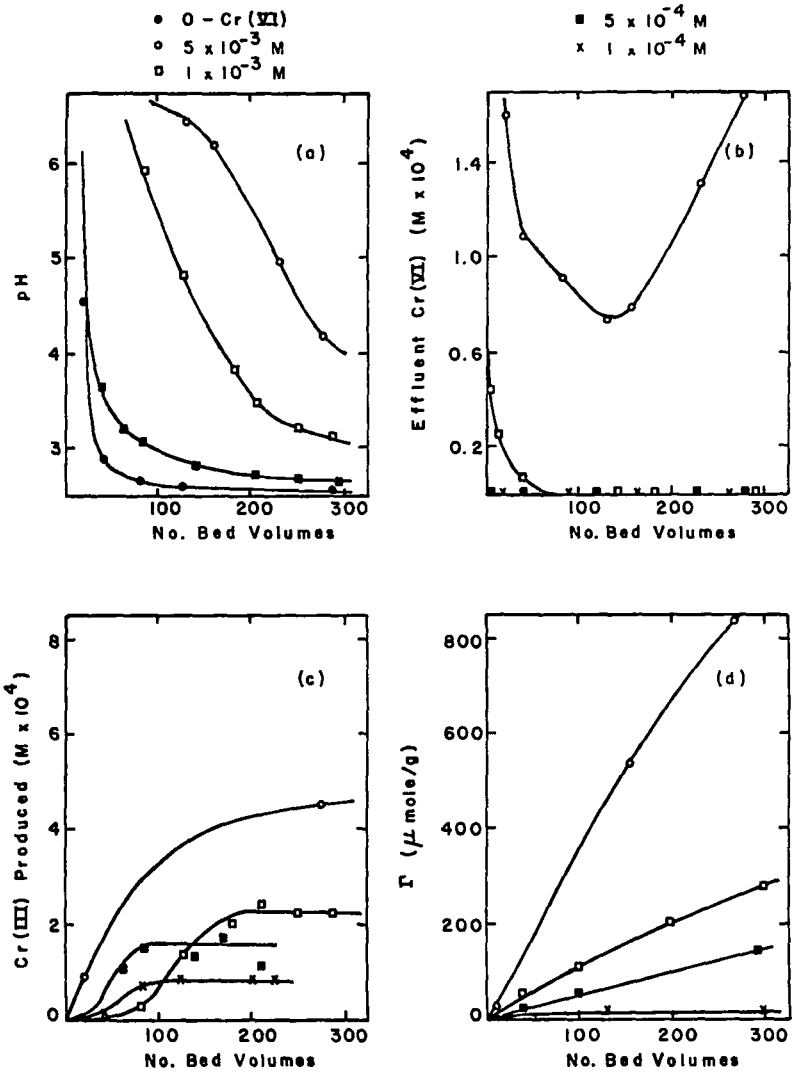

Figure 19. The effect of carbon bed size on:
a. pH
b. residual Cr(VI)
c. Cr(III) produced
d. the Cr(VI) adsorption density.

of 5×10^{-3} M Cr(VI) was never achieved during the entire experiment since the pH remained high (greater than 4 over the entire 300 bed volumes). The H^+ concentration was insufficient to obtain complete removal. Also, the results of Figure 19 (c) show that Cr(III) will still be produced when the influent Cr(VI) to H^+ ratio is greater than one (1.58 for 5×10^{-3} M Cr(VI) to pH 2.50). The 1:1 ratio is generally valid when the Cr(VI) concentration is less than 1×10^{-4} M, or a 1:1 ratio implies the pH is greater than 4.0, which is not a strong reducing condition regardless of the Cr(VI) concentration. Equation 12 shows the reduction rate to depend on the first power of the H^+ concentration. This finding did not agree with what was reported by Kim and Zoltek, who claimed a 1:1 total Cr(VI) to H^+ for minimum reduction and maximum adsorption reactions.

To eliminate the initial Cr(VI) removal deficiency and smooth out the pH in the system, the carbon must be prewashed with an acidic solution before contact with Cr(VI). It is not recommended that a strong acid solution be used for this wash cycle, since strong acids are corrosive to the carbon and may result in a degree of hydrolysis which overshoots the equilibrium that can be obtained by the H^+ concentration in the subsequent wastewater influent. Therefore, the carbon must be hydrolyzed by a wash solution which closely approximates the pH of the influent to be treated. In a column configuration, the wash cycle may be accomplished in approximately 150 bed volumes or less, by a pH of 2.50 or less, as shown previously in Figure 1 (c), while at pH 3.00 or greater, the wash cycle requires too much time and becomes a cumbersome operation. In this case, it may be more convenient to eliminate the concentration gradients which occur in a packed column and hydrolyze the carbon granules by titrating them with acid in a well-mixed reactor until an equilibrium pH is obtained, before placing the carbon into the column.

The results of prewashing with 150 bed volumes of pH 2.50, 0.1 M NaCl washwater before contacting the carbon with Cr(VI) are shown in Figures 20 and 21 for 50 grams of carbon, 5×10^{-4} M and 1×10^{-3} M Na_2CrO_4, respectively, in the influent. The pH is observed to be much smoother over the course of operation and no Cr(VI) was detected in the effluent for 600 bed volumes. The production of Cr(III) was also consistent and increased linearly as the adsorption equilibrium and the progressive increase in Cr(VI) concentration propagated up the column.

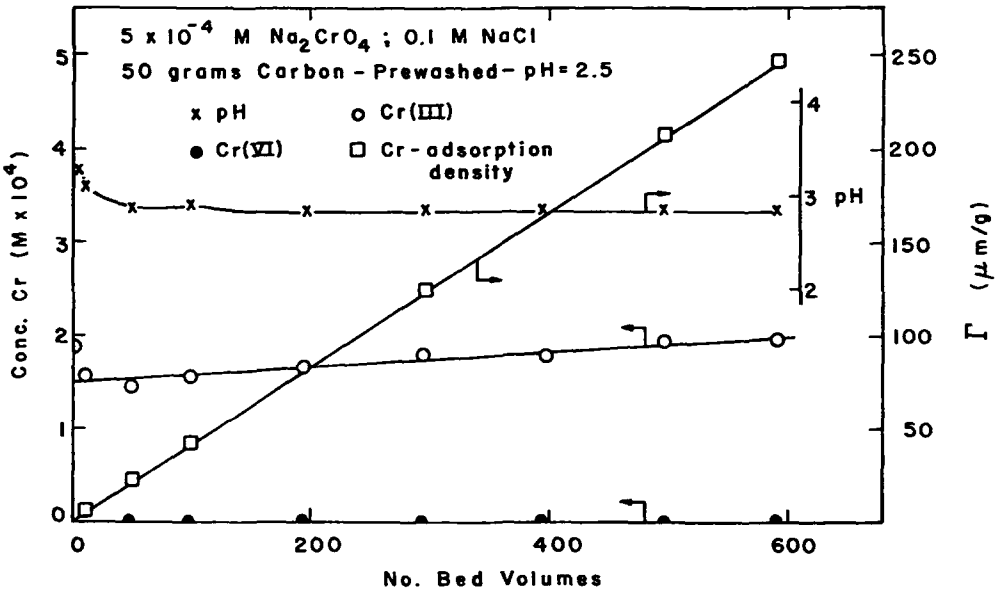

Figure 20. The effluent characteristics of a 5 x 10^{-4} M Na_2CrO_4 (26 ppm Cr(VI)) wastewater after treatment with a prewashed packed column.

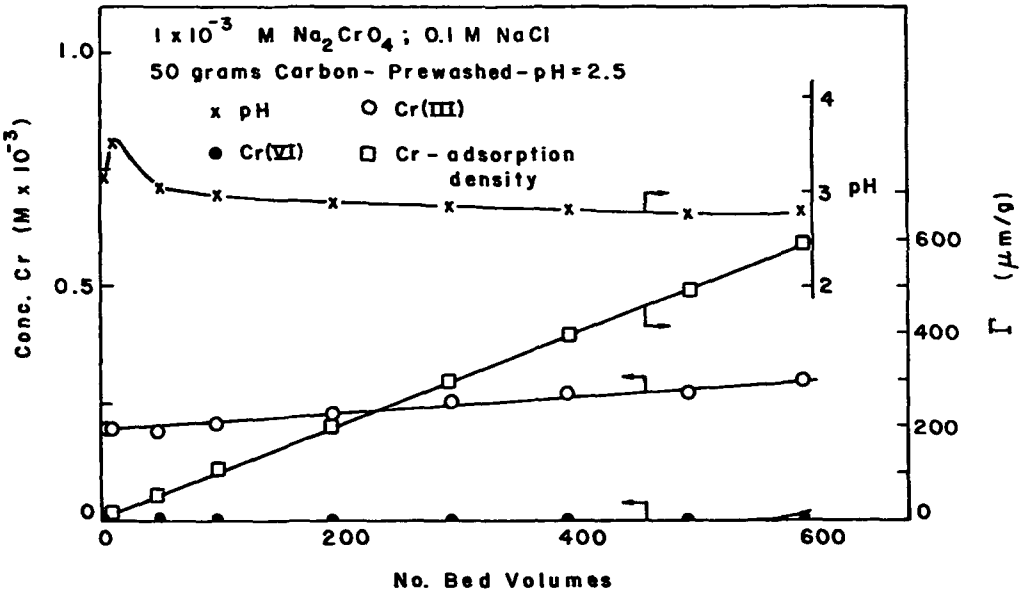

Figure 21. The effluent characteristics of a 1 x 10^{-3} M Na_2CrO_4 (52 ppm Cr(VI)) wastewater after treatment with a prewashed packed column.

Regeneration of Exhausted Activated Carbon

If a full scale system for the removal of Cr(VI) by activated carbon is to be practical or economically feasible, a sound regeneration procedure must be established. Regeneration must perform several functions and meet the following criteria:

1. The removal capacity must not be destroyed by the regeneration process.

2. Chromium must be removed from the carbon surface and concentrated in such a way that the resulting regenerant stream is much more concentrated than the original wastewater stream which was treated.

3. The carbon loss during regeneration must be minimal.

4. The process must be economically feasible.

5. The process should yield no secondary contaminants.

Four methods of regenerating the chromium-laden activated carbon were examined:

1. Thermal regeneration (drying at 103°C in air, 550°C in air or 950°C in CO_2).

2. Caustic regeneration (with NaOH).

3. Combined caustic-thermal regeneration (caustic and 950°C in CO_2).

4. Acid regeneration.

Restoration of Removal Capacity

In the first set of experiments, the carbon was exhaused by subjecting it to nine successive batch adsorption cycles, as described in Section 5, after which the carbon was regenerated and the adsorption cycles repeated. Figure 22 shows the results for the removal of Cr(VI) after regeneration by treating with 1% NaOH, heating in air at 103°C for 24 hours or 550°C for one half hour and heating at 950°C in CO_2 for one half hour, compared with the virgin carbon and a virgin carbon pre-heated at 950°C in CO_2 for one half hour. Thermal regeneration at 950°C, or the combined caustic-thermal techniques, show the same removal capacity and appear to be the most effective, while 1% NaOH is next best and drying in air at 103°C or 550°C appear to create little readsorption capacity. A comparison of the caustic, thermal (950°C in CO_2) and combined caustic-thermal regeneration techniques over several regeneration cycles is shown in Figure 23. Here the combined caustic-thermal technique acquires an advantage over the thermal regeneration alone, and the thermal regeneration approaches the same removal capacity as caustic regeneration as subsequent regeneration cycles are performed.

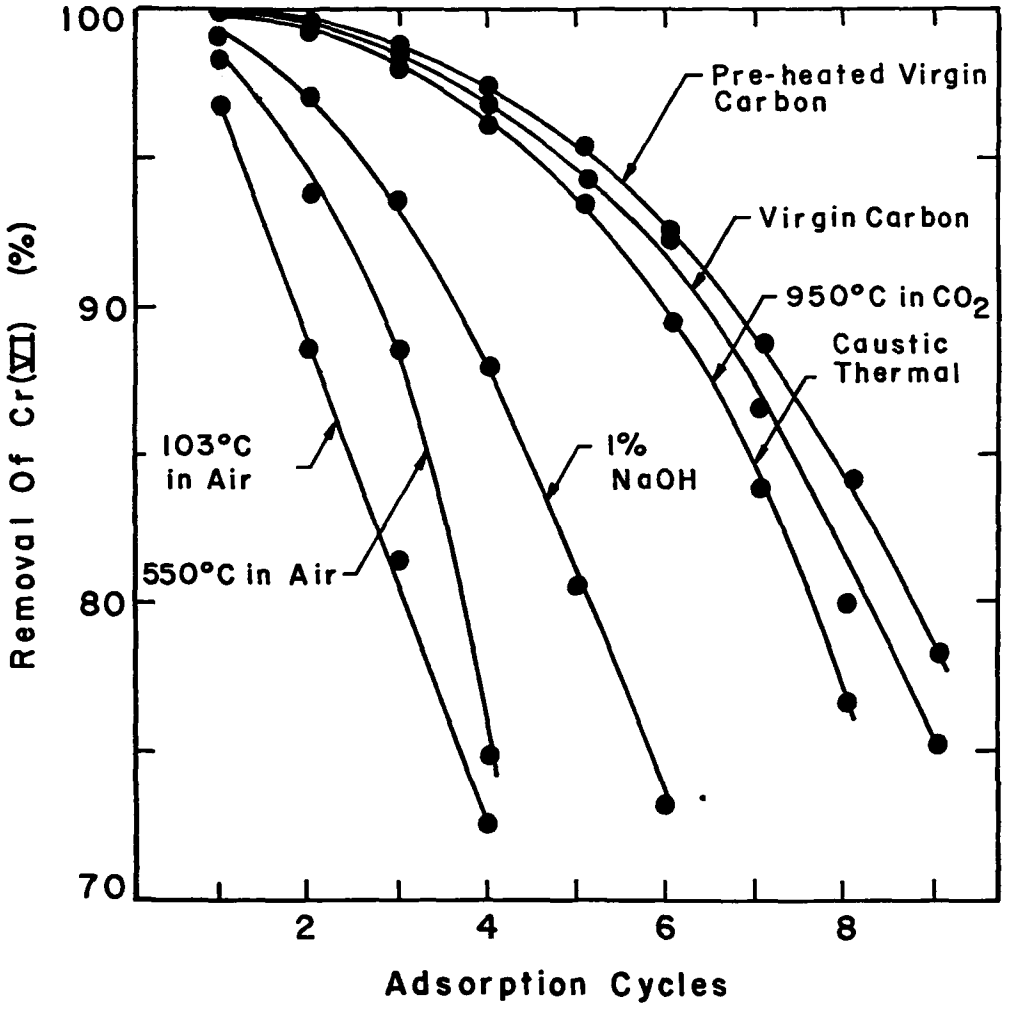

Figure 22. A comparison of Cr(VI) removal capacities following various regeneration techniques.

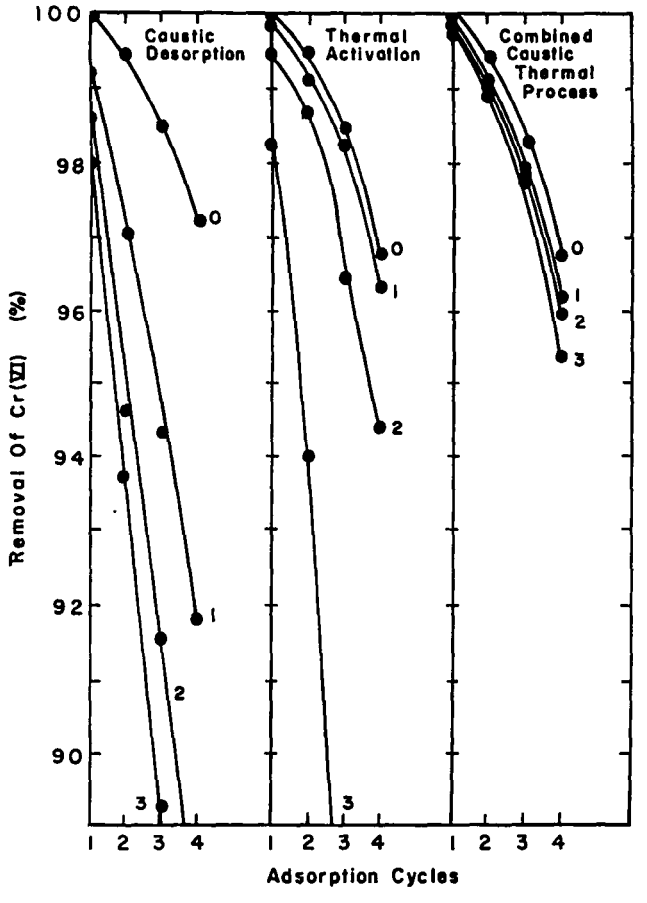

Figure 23. A comparison of regeneration techniques after four adsorption cycles and successive regeneration cycles.

Loss of Carbon

The loss of original carbon due to various physical chemical reactions is shown in Table 8. The average loss of 0.17% carbon by weight during the first adsorption cycle, and another 0.06% loss per additional adsorption cycle, was due mostly to carbon ash. A 1.5% loss of carbon was found when it was treated with 1% NaOH solution. Heating the used carbon in air at 550°C caused the greatest loss of carbon, apparently due to combustion. Thermal activation at 950°C in a CO_2 atmosphere gave a 5% loss of carbon.

TABLE 8. AVERAGE LOSS OF CARBON DURING BATCH ADSORPTION AND REGENERATION

Type of Operation	Average Loss of Carbon per Cycle, % by Weight
First Adsorption Cycle	0.17
Further adsorption cycles	0.06
Caustic regeneration cycle (1% NaOH)	1.50
Thermal regeneration cycle at 550°C in air	7.40
Thermal regeneration cycle at 950°C in CO_2	5.00

Disadvantage of Thermal Regeneration

Even though the thermal regeneration technique appears to be more effective in restoring the Cr(VI) removal capacity, the disadvantages of a thermal regeneration system are significant.

1. Thermal regeneration at 950°C in CO_2 results in a 5% loss of carbon, which translates into significant carbon replacement costs.

2. The costs of building and operating a multiple hearth or fluidized bed furnace at 950°C for regeneration are prohibitive except on a very large scale.

3. The resulting air pollutants, chrome carbonyl or other organo-chromium compounds, which are formed at high temperatures, would require a great deal of additional study and undoubtedly require stringent controls which could be economically and technologically unfeasible.

Therefore, thermal techniques for regeneration of carbons laden with inorganic compounds cannot be an environmentally compatible or economically sound procedure.

Removal of Chromium from the Carbon Surface

In order to evaluate the amount of chromium removed from the carbon surface by regeneration, the original adsorption density and amount of chromium in the regenerate stream must be known. Acid or caustic stripping solutions may be analyzed by standard procedures. However, the analysis of the chromium in the gas flow from thermal regeneration is difficult. Therefore, a procedure for analyzing the amount of chromium directly on the carbon surface may be used. By bombarding elements heavier than sodium with protons, the element can be identified by the wavelength of the resulting x-ray emission and the amount can be determined relative to a reference sample. Since carbon is lighter than sodium, this procedure is ideal for an investigation of heavy

metals on the carbon surface.* Figure 24 shows the x-ray intensity for the chromium emission from the carbon surface after different regeneration techniques were employed.

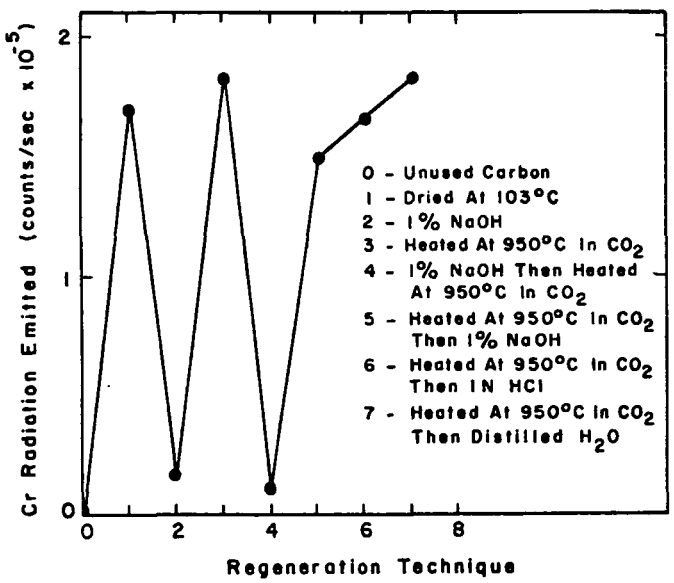

Figure 24. Measure of chromium remaining on the carbon surface by x-ray emission, following various regeneration techniques.

This figure indicates qualitatively that little removal of the chromium adsorbed occurs during thermal regeneration (technique no. 3) compared to caustic regeneration (technique no. 2), and acid or caustic desorption after thermal regeneration (techniques no. 6 and 7) is unsuccessful in removing the adsorbed chromium. Therefore, there is some irreversible chemical reaction which occurs during thermal regeneration which locks the chromium onto the carbon surface.

Caustic Desorption of Adsorbed Chromium

The desorption of chromium from the carbon surface by treatment with caustic solution can be measured directly from chromium analysis of the wastewater treated and the regenerant solution used. Figure 25 shows the percent of chromium desorbed from the carbon surface by various NaOH solutions after successive 24 hour regeneration contact periods with the carbon. Ten grams of carbon were used, which was brought close to equilibrium in a packed column after 1300 bed volumes of influent (1×10^{-3} M Na_2CrO_4, pH 2.50 and 0.1 M NaCl), which was equivalent to an adsorption density of *ca* 940 μm/g. The

* This procedure was developed by Dr. C. M. Fou, University Physics Department, University of Delaware, Newark, Delaware 19711.

carbon was then regenerated in 500 ml of NaOH solution at the indicated strength. If an insufficient amount of Cr(VI) was stripped off after the first contact period, the regenerant was filtered off and placed in a second identical regenerant solution; this was repeated for a third cycle if necessary.

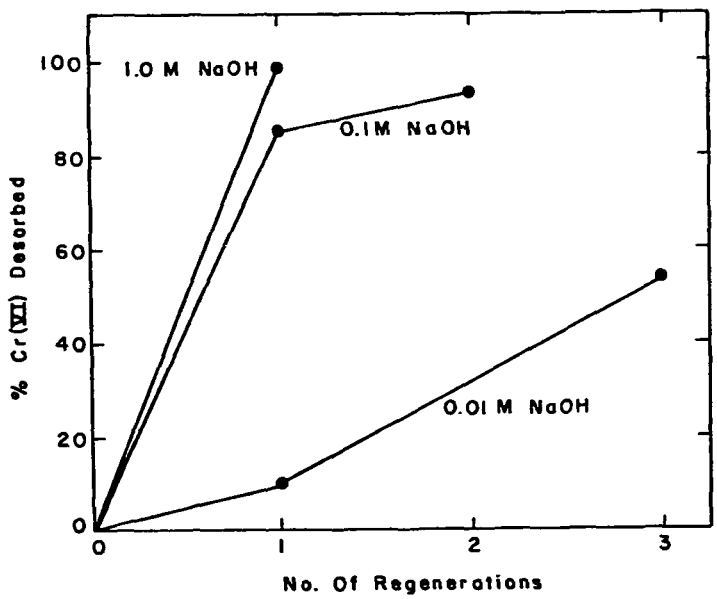

Figure 25. Cummulative percent desorption of chromium from the carbon surface by caustic solution after successive repetitions.

From Figure 25, chromium is more effectively desorbed from the carbon surface as the strength of the caustic solution is increased, but the weaker solutions approach the efficiency of the stronger solutions as the number of regeneration cycles are increased. Therefore, the concentration ratio between chromium in the bulk solution and on the carbon surface increases with the caustic strength. Figure 26 shows the Cr(VI) concentrations reached in the bulk solution for the various caustic solutions during the regeneration cycles. Notice that close to 100% regeneration is achieved by 1.0 M NaOH after 1 cycle for 500 and 250 ml volumes of caustic solution, but the concentration of Cr(VI) is doubled for the solution of lesser volume.

The primary goal of any waste treatment system is to concentrate large volumes of wastewater into a small volume of waste which is easy to handle and dispose of. Therefore, the purpose of regeneration is not only to remove the adsorbed chromium from the surface, but to concentrate that chromium into the smallest regenerate stream possible. Table 9 evaluates the equilibrium Cr(VI) concentrations reached in Figure 26 and shows the percent volume of the regenerant stream compared to the influent stream.

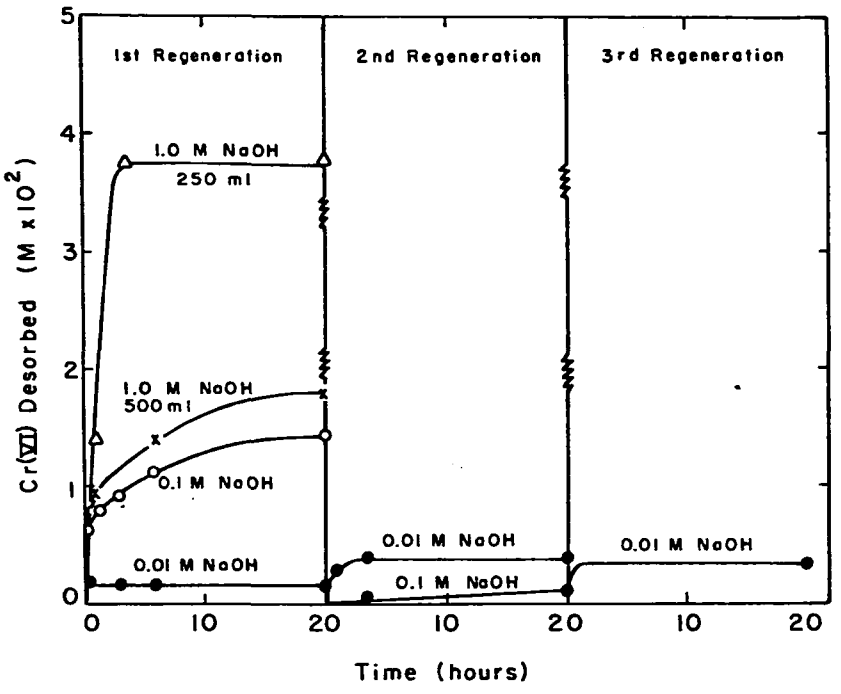

Figure 26. The concentration of Cr(VI) desorbed in caustic solution as a function of time.

TABLE 9. COMPARISON OF WASTEWATER CONCENTRATIONS AND VOLUME REDUCTION WITH STRENGTH OF CAUSTIC REGENERANT STREAM.

[NaOH] (M)	[NaOH] (% by weight)	$[Cr(VI)]_e$ ($M \times 10^{-2}$)	$[Cr(VI)]_e$ (ppm)	Amount Influent* was concentrated (X)	% of Influent* Volume
0.01	0.04	0.37	193	3.7	27.0
0.10	0.40	1.44	749	14.4	6.9
1.00	4.00	3.78	1966	37.8	2.6

* Based on 1×10^{-3} M Na_2CrO_4.

The concentration of Cr(VI) desorbed as a function of NaOH concentration is shown in Figure 27 and can be expressed by the following equation:

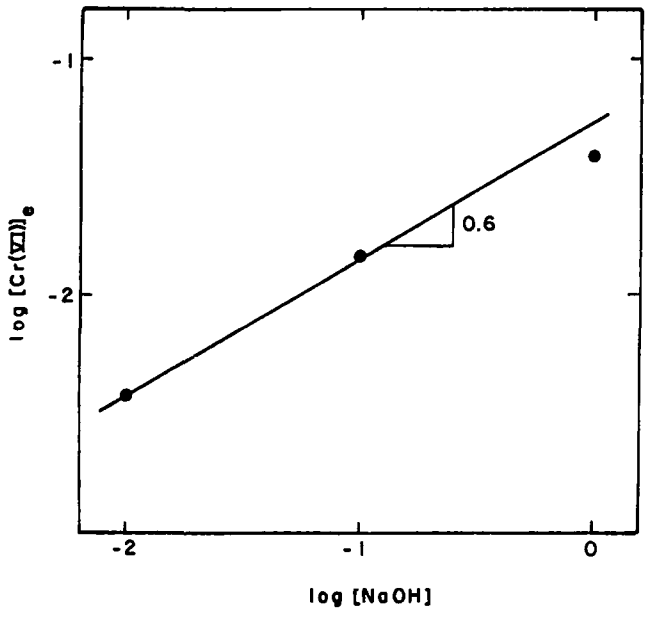

Figure 27. Maximum Cr(VI) concentration in various caustic regenerant solutions.

$$\log [Cr(VI)]_e = 0.6 \log [NaOH]_b - 1.3 \tag{20}$$

and the volume of regenerant solution needed for approximately 100% regeneration of the carbon surface is:

$$\frac{C \times \Gamma \times 10^{-6}}{[Cr(VI)]_e} = V_R \tag{21}$$

where C = mass of carbon (g)

Γ = Cr(VI) adsorption density (μm/g)

$[Cr(VI)]_e$ = equilibrium concentration of Cr(VI) in the bulk NaOH solution calculated from equation 20 (M)

V_R = volume of regenerant solution needed for *ca* 100% Cr(VI) removal (ℓ)

Acidic Desorption of Cr(VI)

Regeneration of the exhausted carbon with strong acid solution appears attractive in an economical sense because acid is generally less expensive than caustic. Figure 28 shows the reduction and desorption of adsorbed Cr(VI) from the carbon surface in 0. 1 M HCl solution. The desorption in the acid solution is much slower than that observed in the caustic regenerate solutions, however, stronger acid solutions might be used to speed up the reaction and increase the extent of desorption. Regeneration with strong acids does have many disadvantages compared to caustic regeneration:

1. The chromium is recovered only in the Cr(III) form; Cr(VI) is not recoverable.

2. The acid regenerant stream must be neutralized with caustic in order to precipitate the $Cr(OH)_3$ species. Therefore, any cost advantage is lost and more caustic must be used than acid.

3. The resultant sludge must be dewatered and disposed of.

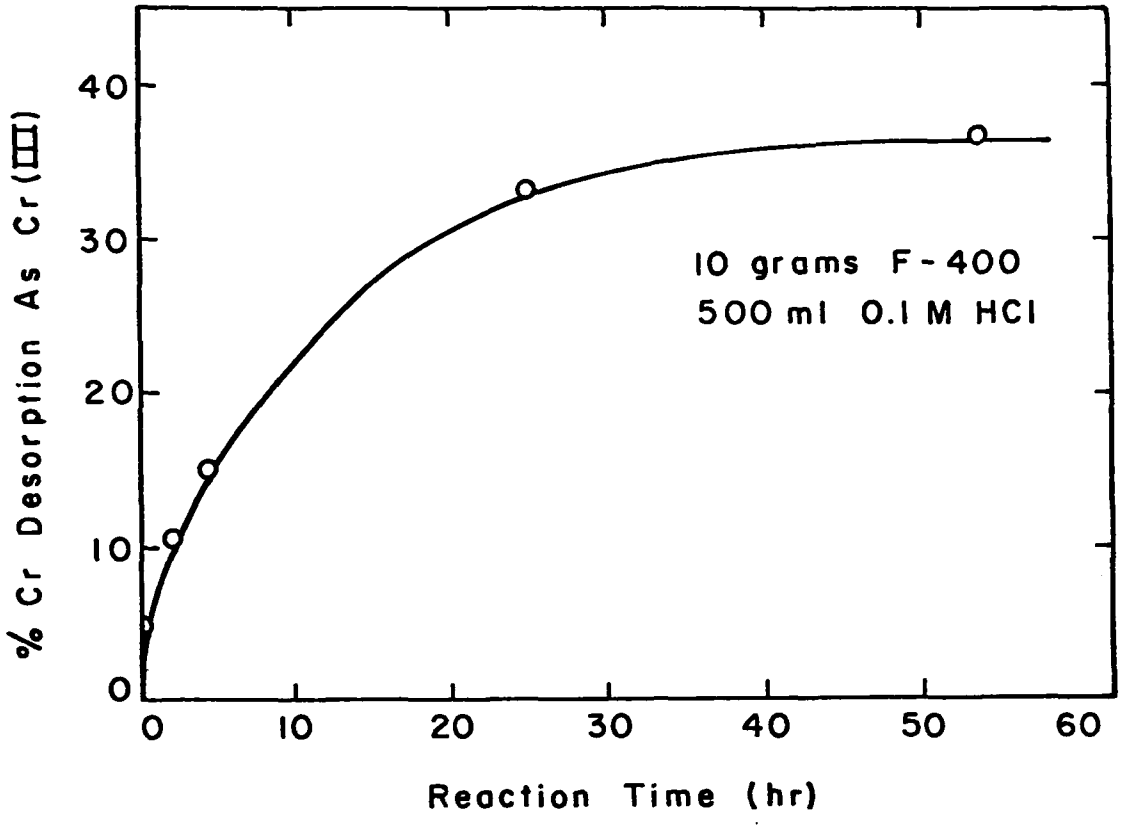

Figure 28. The desorption of Cr(VI) from the carbon surface in acidic solution.

SECTION 7

SYSTEM DESIGN

The removal of Cr(VI) from wastewater by an activated carbon process involves reduction and adsorption of the Cr(VI) species occurring simultaneously. Based upon the results obtained in this research, two types of treatment schemes may be suggested:

1. That the reaction parameters are manipulated to favor the adsorption of Cr(VI) to the extent that no significant amount of Cr(III) will be produced.

2. That the reduction of Cr(VI) is allowed to occur and a subsequent treatment scheme is utilized to remove the Cr(III) which has been produced.

From the previous kinetic studies, the major reaction parameters for reduction and adsorption were found to be pH, degree of mixing or velocity gradient (G), carbon dose ([C]), and total Cr(VI) concentration. By comparing the kinetic expressions for reduction and adsorption (Equations 11 and 17), the most effective parameters governing the ratio of reduction rate to adsorption rate ($R_{red}:R_{ads}$) are pH and G. From Equation 11, it is seen that $R_{red} \alpha [H^+]$ and G; while Equation 17 shows $R_{ads} \alpha [H^+]^{0.2}$ and is independent of G over a normal range of mixing.

Figure 29 shows the rates of reduction and adsorption ($M\text{-}min^{-1}$), calculated from Equations 11 and 17, assuming constant values for $[HCrO_4^-]$, [C], and [Cr(III)] = 0, at various values of G (for the reduction rate) and π (for the adsorption reaction) as a function of solution pH.

From Figure 29, the adsorptive removal becomes dominant as the pH in the bulk solution is increased. However, the adsorption rate decreases as the carbon approaches maximum capacity ($\pi \rightarrow 1.0$) and the reduction reaction will dominate when π becomes sufficiently close to 1.0. Therefore, if the treatment process is to be operated in an adsorption-controlled mode, with little Cr(III) produced, i.e., $R_{red}:R_{ads} \simeq 0$, then the wastewater must be contacted with the carbon in a completely mixed type reactor; then π can be controlled by the residence time of the carbon in the reactor. In contrast to this, the initial layers of carbon approach equilibrium rather quickly in a packed column reactor. The resulting concentration gradient along the column is utilized to optimize the adsorption density and thereby fully utilize the carbon capacity to the fullest extent.

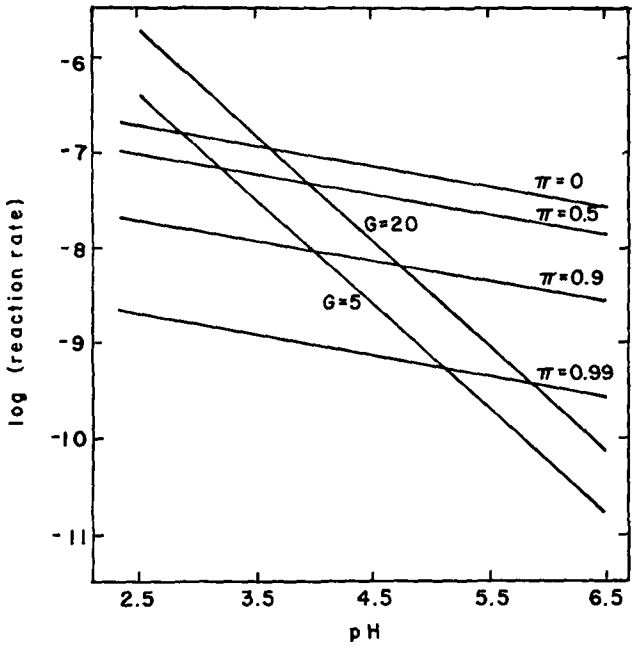

Figure 29. The rates of reduction and adsorption (mole/ℓ-min) as functions of pH, G and π*, for [C] = 2 g/ℓ, $[HCrO_4^-]$ = 1.0×10^{-5} M and [Cr(III)] = 0.

* $\pi = \frac{\Gamma}{\Gamma_e}$ = 0 initially and approaches 1 as total adsorption capacity is reached.

SYSTEM 1 - TREATMENT BY ADSORPTION IN A COMPLETELY MIXED REACTOR (CMR)

A CMR offers the advantage of simplifying the control on all the reaction parameters for reduction and adsorption. The variables which may be selected for the design of a CMR system are:

1. The velocity gradient in the reactor, G (sec^{-1}).

2. The solution pH in the reactor.

3. The carbon dose in the reactor, [C] (g/ℓ).

4. The extent of the carbon adsorptive capacity maintained, π.

5. The ratio of reduction rate to adsorption rate, R_{red}/R_{ads}.

The simplest way to restrict R_{red}/R_{ads} is by controlling the velocity gradient in the reactor. Since $R_{red} \propto G$, the lowest possible value of G is

desirable as long as R_{ads} is not effected. Therefore, G = 5 sec^{-1} has been selected for all design calculations in this system.

Figure 30 shows R_{red}/R_{ads} at several values of π and G = 5.0 sec^{-1} as a function of pH. Figure 30 also indicates the need to operate at an increasingly high pH value to maintain a small ratio of R_{reds} to R_{ads} as π increases. The dependence of π on pH to maintain a constant R_{red}/R_{ads} is shown in Figure 31. Therefore, from Figure 31, the minimum pH or maximum π value for any R_{red} to R_{ads} ratio may be determined. To insure that the production of Cr(III) is insignificant, a value of R_{red}/R_{ads} of at most 1:50 is necessary. To meet this criteria, the pH in the reaction vessel must be greater than *ca* 4.8 (from Figure 31). Many combinations of pH and π may be chosen to satisfy the recommended value of R_{red}/R_{ads}, however, several constraints on choosing the proper pH and π values must be considered:

1. Is the Cr(VI) capacity of the desired carbon dosage, at the pH and π value, large enough to accommodate the Cr(VI) which must be removed from the wastewater?

2. Are the kinetics of adsorption fast enough to insure the desired removal in a reasonable reactor size?

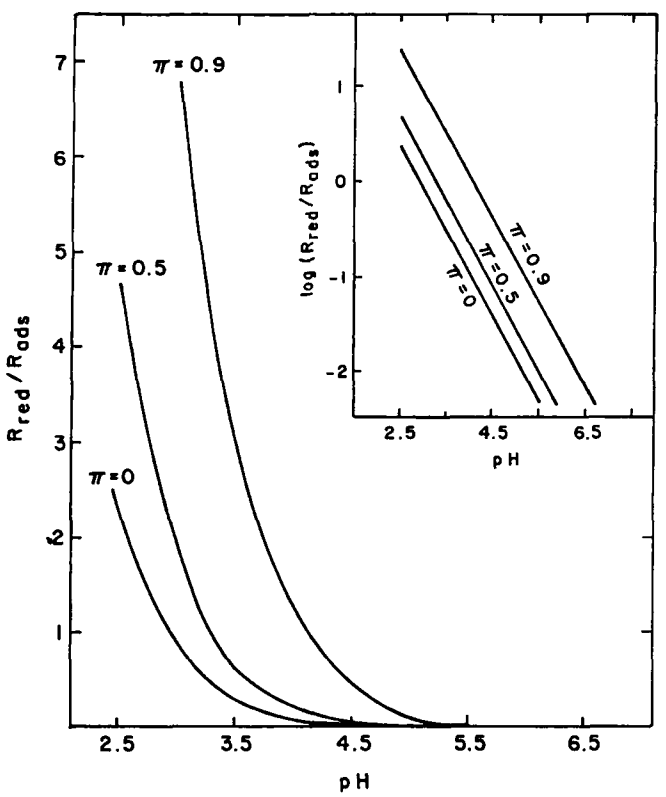

Figure 30. The ratio of R_{red} to R_{ads} as a function of pH (calculated from Figure 29).

The Cr(VI) adsorptive capacity of the carbon can be determined from Equations 13 and 14 and the adsorption density on the carbon in a reaction vessel at any pH and π can be evaluated as:

$$\Gamma = \pi \, \Gamma_e \tag{22}$$

where Γ = adsorption density in the reactor (μ mole/g).

π = fraction of adsorptive capacity chosen from Figure 31.

Γ_e = maximum adsorptive capacity calculated from Equations 13 and 14 (μ mole/g).

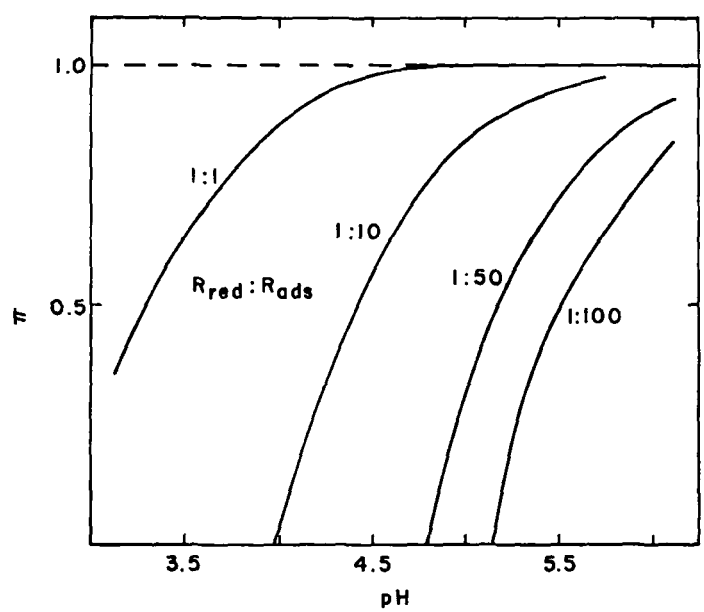

Figure 31. π vs. pH over equal values of R_{red}/R_{ads} ratios.

The minimum carbon dosage required for treatment in one or more CMR is:

$$[C]_{min} = \frac{[Cr(VI)]_o \times P \times 10^4}{\Gamma} \tag{23}$$

where $[C]_{min}$ = minimum carbon dosage required (g/ℓ).

$[Cr(VI)]_o$ = Cr(VI) concentration in the wastewater before treatment (M).

P = percentage of Cr(VI) removal desired (%).

Γ = desired adsorption density in the head reactor calculated from Equation 22 (μ mole/g).

The minimum carbon dose required to maintain a 1:50 R_{red}/R_{ads} ratio for 99% Cr(VI) removal from a 1 x 10^{-3} M Na_2CrO_4 (52 ppm Cr(VI)) wastewater solution as a function of pH and Cr(VI) concentration in the head reactor are shown in Figure 32.

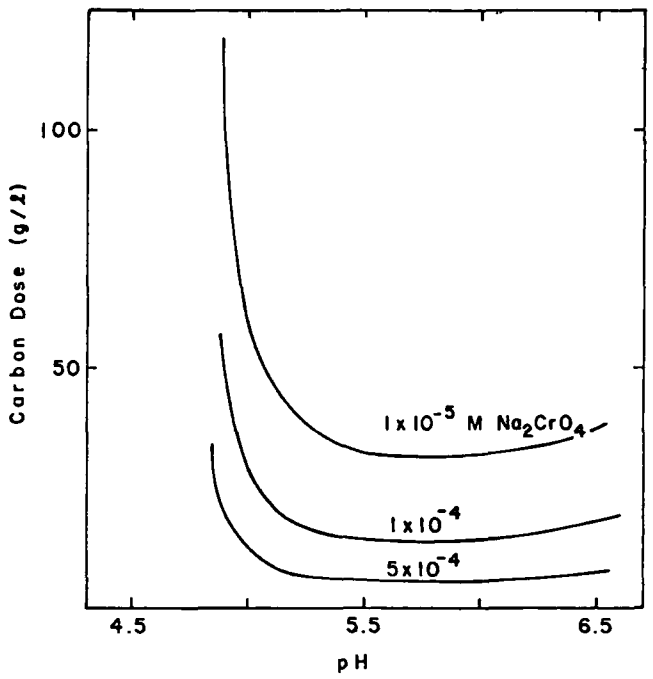

Figure 32. The carbon dose required for 99% treatment of a 1 x 10^{-3} M Na_2CrO_4 solution as a function of pH and Na_2CrO_4 in the head reactor.

The carbon dose is high at the lower pH range due to the lower π values necessary to maintain R_{red}/R_{ads} = 1:50. The absolute minimum dosage occurs over a fairly flat region between pH 5.2 to 6.5.

The carbon dosage also decreases as the concentration of Cr(VI) in the reactor increases, due to the high adsorptive capacities (Γ_e) at high concentrations. This in turn indicates that the carbon may be used more efficiently if more than one reactor in series is used (i.e., continuous countercurrent operation).

Case Study - Continuous Completely-Mixed Reaction System

A great number of system designs may be used, all of which are capable of providing the same degree of treatment, however, it is the cost of these individual designs which will determine the best or optimal solution to the wastewater treatment. In order to evaluate the economics of operating at different pH, carbon dose or π values, the cost associated with the size of the reactor needed and the cost of the carbon used by the system, must be determined.

In order to optimize these operational variables, a hypothetical case was considered as follows:

Wastewater flow = 10,000 gal/day

[Cr(VI)] = 1×10^{-3} M (52 ppm)

Removal percentage = 99%

$R_{red}:R_{ads}$ = 1:50

System operation = 8 hrs/day and 300 days/year

Capital costs are amortized over 10 years at an interest rate of 8% (i.e., capital recovery factor = 0.149)

Filtrasorb 400 = 61¢/lb in bulk rates

Considering the corrosiveness of the Cr(VI) wastewater, the best material for the reaction vessel would be fiberglass. A rough survey of costs for large fiberglass tanks indicates that:

$$\log (C.C.) = 0.8 \log (V) + 0.63 \qquad (24)$$

where:

C.C. = capital cost of a fiberglass tank ($)

V = volume of the reaction vessel (gal)

By neglecting the reduction of Cr(VI) species and assuming that all Cr(VI) removal will occur through adsorption, the reactor volume needed for a single reactor, or each vessel in a series of equal sized reactors, can be found by applying a mass balance to the system at a steady state and using Equation 18 for the rate of adsorption, or:

$$V = \frac{7.11 \times 10^{-1} \left(\frac{P}{100-P}\right) \Gamma_e}{[H^+]^{0.2} \left(\frac{1}{\pi} - 1\right)} \qquad (25)^*$$

where:

V = volume of each reactor (gal)

Γ_e = maximum adsorptive capacity at given pH and Cr(VI) concentration in the reactor, calculated from Equations 13 and 14 (μ mole/g)

$[H^+]$ = hydrogen ion concentration (M)

π = fraction of adsorptive capacity

P = percentage of Cr(VI) removal in each reactor (%)

and P may be calculated for any number of equal sized vessels in series:

$$P = 100 - \left\{ \left(\frac{100 - P_T}{100}\right)^{\frac{1}{n}} \times 100 \right\} \qquad (26)$$

where:

P_T = total removal efficiency of the entire treatment train (%)

n = number of vessels in series (n = 1, 2, 3...)

Evaluation of pH for Cost-Effective Adsorption of Cr(VI)

It has been determined previously that an effective treatment system must operate with at least 1:50 $R_{red}:R_{ads}$ ratio, which restricts the maximum π value (π_{max}) at different pH's as shown by Figure 31. In turn, the required carbon dosage is affected by π_{max} as shown in Equation 23 and the reactor volume is fixed by the pH, carbon dose and π value. Therefore, the trends indicate an increase in capital costs due to the increased vessel size as the pH and π values increase, while the operating costs due to carbon usage decrease to a minimum with the carbon dosage as shown in Figure 32. A comparison of reaction vessel sizes and costs at various allowable pH's and $\pi < \pi_{max}$ are shown in Table 10.

* Derived by substituting $[C] = \frac{1,000}{\pi \Gamma_e}$ into Equation 18 (applies for 1×10^{-3} M Cr(VI) only).

TABLE 10. REACTOR SIZE AND ESTIMATED COSTS ASSOCIATED WITH THE REACTOR VOLUME AND APPLIED CARBON DOSE FOR A SINGLE CMR.

pH	π	V* (gal)	C† (g/ℓ)	C.C.‡ ($)	Cost of Carbon§ (¢/gal)
4.88	0.05	1,960	357	1,840	3.58
	0.10	4,140	179	3,340	1.80
	0.15	6,570	119	4,830	1.20
5.0	0.1	4,140	189	3,340	1.90
	0.2	9,300	95	6,380	0.95
	0.3	15,970	63	9,830	0.64
5.25	0.1	4,130	212	3,340	2.13
	0.3	15,940	70	9,830	0.70
	0.5	37,200	43	19,340	0.43
5.50	0.1	4,130	238	3,340	2.38
	0.4	24,810	60	13,983	0.60
	0.6	55,810	40	26,750	0.41
	0.7	86,860	34	38,110	0.35
6.0	0.1	4,140	299	3,340	3.00
	0.4	24,840	75	13,980	0.75
	0.6	55,890	50	26,754	0.50
	0.9	335,210	33	112,266	0.33

* Volume calculated from Equation 25 assuming P = 99%.

† Carbon dose calculated from Equation 23.

‡ Capital cost calculated from Equation 24.

§ Based on 2% carbon loss during use and regeneration at 61¢/lb Filtrasorb 400.

The assumed carbon cost was based on a 2% loss of carbon after each cycle of use. The complete summary of total treatment cost due to amortized capital costs over 10 years at 8% interest rate and operating expense due to the carbon loss, is shown in Figure 33. The graph shows that the most economical design for a single reaction vessel occurs at pH 5.25 and π = 0.55. The total treatment cost is 0.52¢/gal or $52/day ($15,600/year) for a 10,000 gal/day operation.

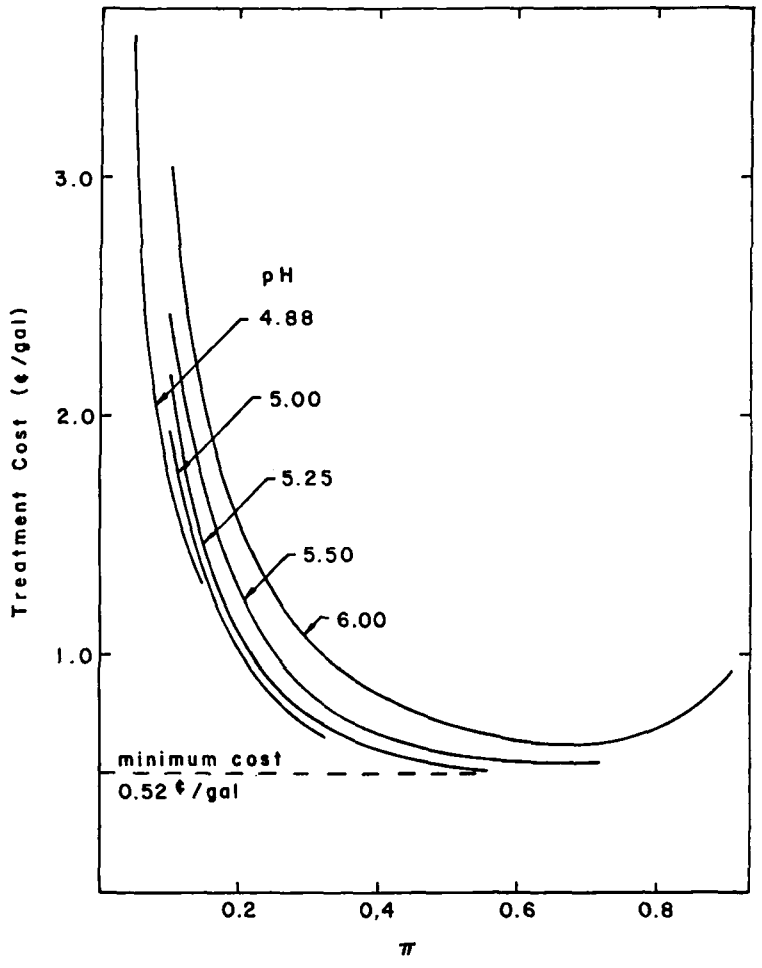

Figure 33. Treatment costs in a single complete-mix contact vessel at various pH's as a function of π.

Equal Sized Reactors in Series

From Table 10, the most significant portion of the treatment cost results from replenishing the carbon supply. This cost accounts for 77% of optimal treatment cost at pH 5.25. In a series of CMR's, the steady state concentration of Cr(VI) in each reactor is larger than the Cr(VI) concentration of the following reactor in the series. Therefore, by using a series of CMR's and cycling the used carbon from the tail reactor to the head end of the system before regenerating, the step-ups in Cr(VI) concentration can be utilized to increase the carbon adsorptive capacity (Γ_e) and thereby decrease the carbon dosage needed for treatment. As the number of CMR's in series increases, the system will gradually approach the carbon efficiency of a packed column and the treatment cost associated with the carbon dose will approach a minimum. The series of reactors also reduces the reactor volume needed to achieve

the same degree of treatment. Capital costs for 1, 2, 3, and 4 reactors in series were estimated using Equations 25 and 26 for the volume of each reactor and Equation 24 (less 10% for more than one vessel) plus an additional $3,000 for extra equipment, such as pumps, pH controls, carbon separators and mixers, on each additional reactor. Carbon costs were estimated by assuming 2% loss per cycle. Figure 34 compares the total treatment costs and indicates that the cost can be decreased to *ca* 0.20¢/gal at π = 5.5 for 4 reactors in a series. However, the difference between 3 and 4 reactors appears insignificant 0.21¢/gal vs. 0.20¢/gal, and the increased complexity of the system for each additional reactor would indicate that 3 reactors would be the optimal design at a cost of 0.21¢/gal or $21/day.

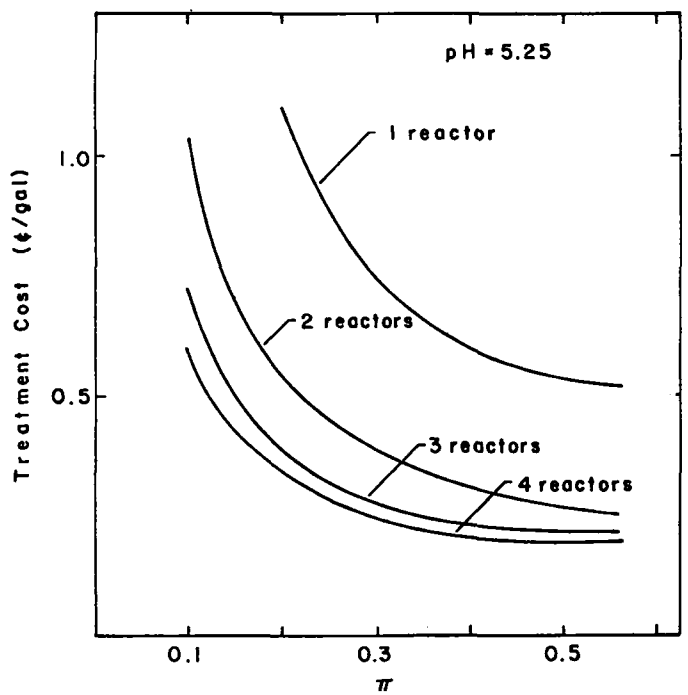

Figure 34. Comparison of treatment costs for multiple reactors in series.

SYSTEM 2 - COLUMN OPERATION

Column operation is more efficient than a completely mixed reactor, due to the fact that a column fully utilizes the carbon adsorption capacity due to a large concentration gradient existing opposite to the direction of flow in the column. Therefore, Cr(VI) adsorption may be less expensive in a column if a subsequent treatment system is employed to remove the Cr(III) which has been produced.

Column operation is sensitive to the pH in the wastewater influent stream, since there is a stoichiometric requirement of one mole of H^+ per mole Cr(VI) adsorbed and 4 moles of H^+ per mole Cr(VI) reduced. In order to

completely remove all of the Cr(VI) from solution, a 1:1 molar ratio of H^+ to Cr(VI) would be the absolute minimum ratio of H^+:Cr(VI), if Cr(VI) was removed exclusively by adsorption. In fact, an excess of H^+ is required to satisfy the stoichiometric demand of H^+ for reduction and to prevent the decreased H^+ concentration in the latter portions of the column from limiting the removal rates and diminishing the Cr(VI) adsorptive capacity of the carbon.

For a case study similar to the one presented previously, i.e., 1×10^{-3} M Cr(VI), the maximum pH in the influent would be 3.0. However, an excess of H^+ is desired and the maximum Cr(VI) adsorptive capacity of the carbon occurs at *ca* pH 2.50 (1,280 μ moles Cr(VI)/g). Bench scale experiments have also indicated excellent Cr(VI) removal performance at this pH value (Figure 19). Therefore, pH 2.50 appears to be the optimum condition for complete removal of Cr(VI) by adsorption and reduction.

The surface loading rate of the carbon columns in this study has been 2 gal/min/ft^2. Therefore, at a wastewater flow rate of 10,000 gal/day operating 8 hr/day, the column would require 10.4 ft^2 of surface area or be 3.64 ft in diameter.

The depth of the column can be estimated from experimental data. Table 11 shows the experimental bed size and the number of influent bed volumes passed through each column before breakthrough occurred.

TABLE 11. COLUMN DEPTH VERSUS NUMBER OF BED VOLUMES TO Cr(VI) BREAKTHROUGH*

Bed Size (grams)	Bed Depth (ft)	Number of Bed Volumes to Breakthrough
10	0.14	125
30	0.42	400
50	0.70	600

* Flow rate = 2 gal/min/ft^2; pH_o = 2.5; total $Cr(VI)_o = 1 \times 10^{-3}$ M

A log plot of bed volumes versus bed depth is shown in Figure 35. The number of bed volumes may then be written as a function of bed depth or:

$$\log (BV_b) = 0.92 \log (d_b) + 2.94 \qquad (27)$$

where:

BV_b = number of bed volumes to breakthrough

d_b = carbon bed depth (ft)

The depth of the bed needed for a system can be evaluated by choosing the desired time interval between regenerations, which implies:

$$BV_b = \frac{Qt}{7.48\ (SA)d_b} \tag{28}$$

where:

Q = wastewater flow rate (gal/day)

t = time interval between regenerations (days of actual system operation)

SA = Column surface area perpendicular to the flow (ft^2)

Q, t, and SA should all be known, from which d_b can be derived by solving Equation 27. By assuming 10,000 gal/day with regeneration cycles once a month (22 days of actual operation), d_b = 2.4 ft. Therefore, a 4 ft diameter by 3 ft depth carbon bed would be a conservative design and require 1,082 lb of carbon. Therefore, regenerating once a month at a 2% carbon loss means the replacement cost for the column would be 0.01¢/gal. The column operation offers a significant advantage over the continuous flow system where the carbon operating cost was 0.12¢/gal at pH 5.25 and π = 5.5 using three reaction vessels.

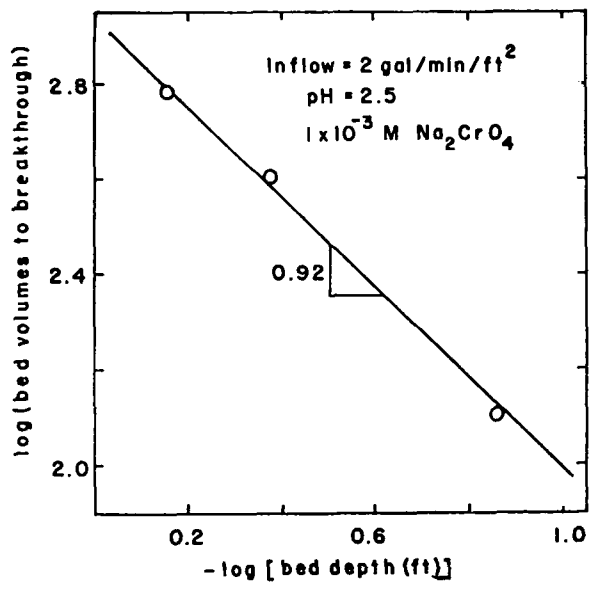

Figure 35. Bed volumes to breakthrough as a function of carbon bed depth for 1 x 10^{-3} M Na_2CrO_4 at pH 2.50.

The initial column must be followed by a Cr(III) treatment system capable of treating 10,000 gal/day with 2.0 to 3.0 x 10^{-4} M Cr(III) (see Figure 19). Although no data on the adsorption of Cr(III) by activated carbon has been presented in this report, it is believed that a comparable system for its removal might be developed and operated at about the same cost as the Cr(VI) adsorption column and the total carbon cost might be 0.02 to 0.03¢/gal for complete adsorption of all chromium species from solution.

It is also relevant to compare the cost of using activated carbon for Cr(VI) reduction to the cost of conventional reduction with sulfur dioxide (SO_2). The following unit material costs can be attributed to each:

Filtrasorb 400 costs 61¢/lb or \$61/100 lb

SO_2 costs \$8.51/100 lb

From the stoichiometry of the reduction reactions:

1. for Cr(VI) reduction by carbon, Equation 9 implies that three moles of carbon is required to reduce four moles of Cr(VI)

2. for Cr(VI) reduction by SO_2 the following stoichiometry applies:

$$2\ H_2CrO_4 + 3\ SO_2 \rightleftarrows Cr_2(SO_4)_3 + 2\ H_2O$$

or three moles of SO_2 is required per two moles of Cr(VI) reduced.

Therefore, assuming 100% efficiency of reaction, for 10,000 gal of 1 x 10^{-3} M Na_2CrO_4 per day, to completely reduce all of the Cr(VI), the chemical costs would be 51¢/day for SO_2 and 46¢/day for Filtrasorb 400. Therefore, it is favorable to use activated carbon for reduction of Cr(VI) in solution compared to currently used reducing agents.

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APPENDIX

AQUEOUS CHEMISTRY OF CHROMIUM

Chromium is a highly active transition metal which exists in several oxidation states from the divalent to hexavalent form. However, the major stable aqueous species are either in the hexavalent or trivalent state (1). The stability of the various chromium species is dependent upon the various reducing, oxidation and pH conditions. Figure A-1 shows the stable domains for various chromium species in aqueous systems as affected by the oxidation potential (E_h) and pH (34). Under the pH (< 3), temperature (20-30°C) and reducing-oxidizing conditions commonly found in industrial wastewaters, the predominant species are bichromate, $HCrO_4^-$, dichromate, $Cr_2O_7^{-2}$, and Cr^{+3}. It is interesting to note that the divalent chromium ions, Cr^{+2}, may be found in extremely reducing environments.

The constitution of hexavalent chromium in the wastewater includes several common hexavalent chromium anions; namely, (a) the hydrochromate or bichromate monovalent anion, $HCrO_4^-$; (b) the anhydride of the acid chromate ion, the divalent dichromate anion, $Cr_2O_7^=$; and (c) the divalent chromate anion, $CrO_4^=$ (35). The equilibria of various Cr(VI) species are shown as follows (36):

$$CrO_4^{-2} + H^+ \rightleftarrows HCrO_4^- \quad ; \quad \log k_1 = 6.5$$

$$HCrO_4^- + H^+ \rightleftarrows H_2CrO_4 \quad ; \quad \log k_2 = -0.8$$

$$2\ HCrO_4^- \rightleftarrows Cr_2O_7^{-2} + H_2O \quad ; \quad \log k_3 = 1.52$$

$$Cr_2O_7^{-2} + H^+ \rightleftarrows HCr_2O_7^- \quad ; \quad \log k_4 = 0.07$$

Based upon the above equilibria, the distribution of various Cr(VI) species as a function of pH and concentration can be computed and the fraction of the total Cr(VI) species which is in the $HCrO_4^-$ form under most conditions can be written quantitatively as:

$$\alpha_1 = \frac{-\left\{1 + \frac{10^{-6.5}}{[H^+]}\right\} + \left\{\left(1 + \frac{10^{-6.5}}{[H^+]}\right)^2 + 1.33 \times 10^2\ [Cr_T]\right\}^{\frac{1}{2}}}{66.3\ [Cr_T]} \qquad (29)$$

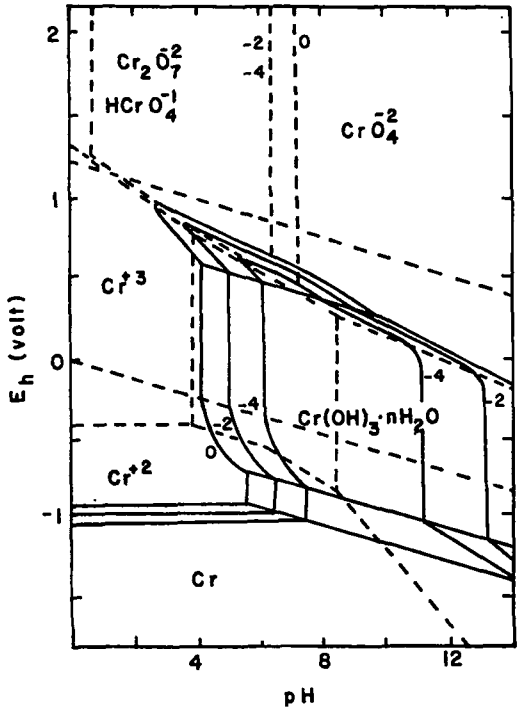

Figure A-1. The stability diagram of chromium species in aqueous solution at 20°C, after Pourbaix (34), as function of E_h and pH. The values of 0, -2, -4 designate - log (Cr_T - molar).

where:

α_1 = the fraction of Cr(VI) species which are $HCrO_4^-$

$[H^+] = 10^{-pH}$ (M)

$[Cr_T]$ = total Cr(VI) in solution (M)

The concentration distribution between $HCrO_4^-$ and $Cr_2O_7^{-2}$ is largely governed by the total Cr(VI) present. As indicated in Figure A-2 (36), the fraction of $Cr_2O_7^{-2}$ only becomes significant at high concentration of total Cr(VI). Figure A-2 also shows the distribution of Cr(VI) species as function of pH for total Cr(VI) covering from 10^{-4} M to 6 x 10^{-3} M (or 5.2 to 312 ppm as Cr), an average concentration range which generally occurs in most industrial wastewaters (5).

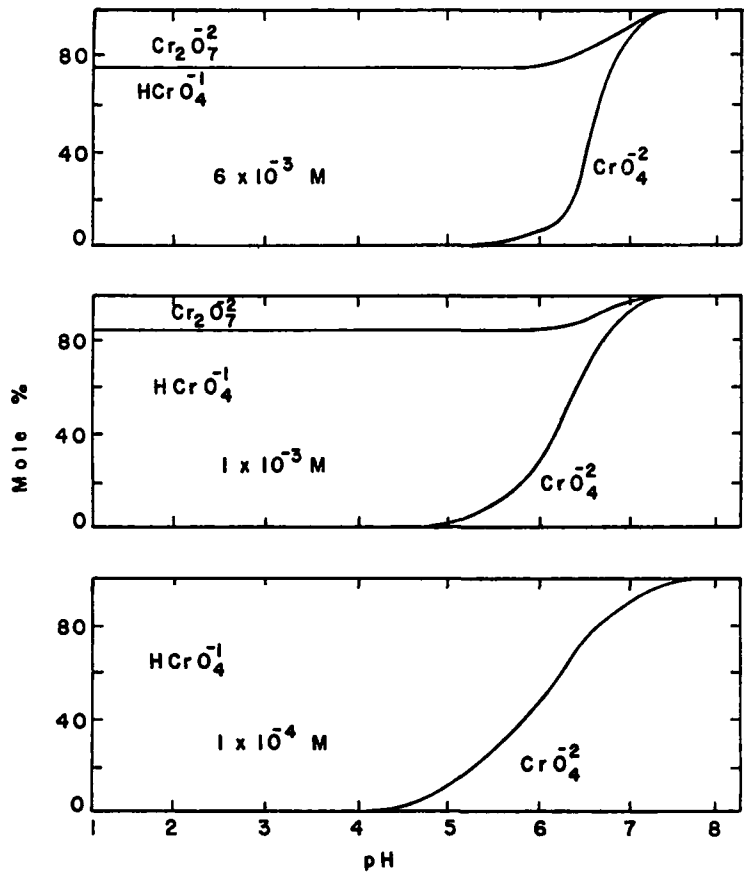

Figure A-2. The molar distribution of the Cr(VI) species as function of pH and total Cr(VI). (Recalculated from Stumm and Morgan)(36).

When present in a trivalent state, the dominant solid form is $Cr(OH)_3(s) \cdot nH_2O$ which is not very soluble. The solubility of trivalent chromium hydroxide is minimum at pH 8.5 (≈ 0.02 ppm) and increases to 520 ppm at pH 5. Figure A-3 shows the effect of pH on the solubility of $Cr(OH)_3(s) \cdot nH_2O$.

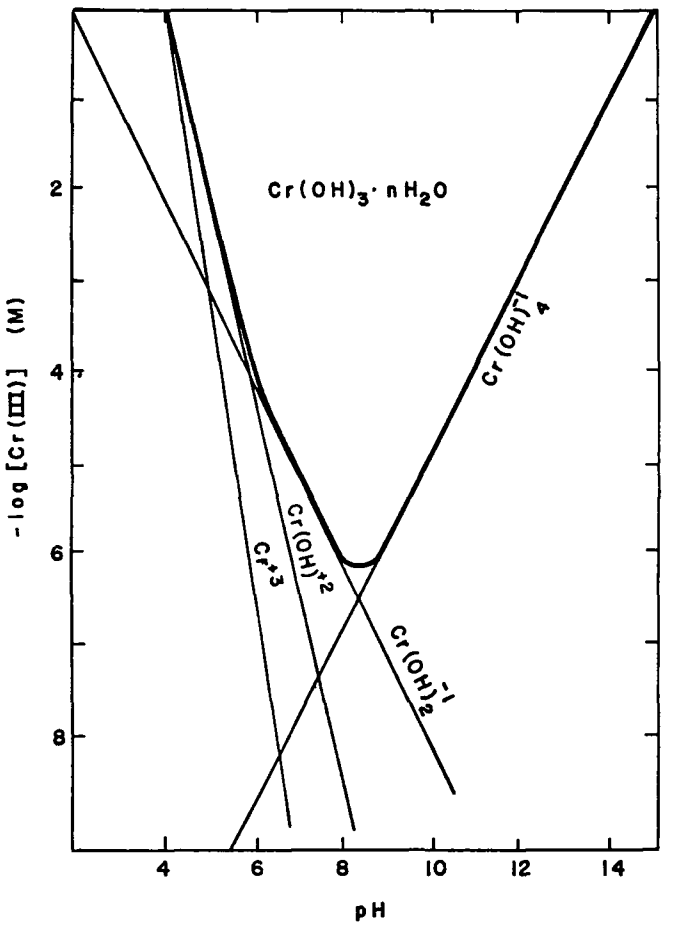

Figure A-3. The concentration distribution of various Cr(III) species as governed by the solubility of solid $Cr(OH)_3 \cdot nH_2O$, after Pourbaix (34).

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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16. ABSTRACT

The removal of hexavalent chromium, Cr(VI), from dilute aqueous solution by an activated carbon process has been investigated. Two removal mechanisms were observed: hexavalent chromium species were removed by adsorption onto the interior carbon surface and/or through reduction to the trivalent state at the external carbon surface.

The effects of Cr(VI) concentrations, pH, carbon dosage and extent of mixing in the reaction vessel were studied in the batch mode and in continuous flow packed column experiments in the laboratory. The adsorptive capacity of the carbon and the rates of Cr(VI) adsorption and reduction have been determined.

Thermal regeneration of the exhausted carbon was examined, along with caustic or acid stripping solutions and a combined caustic-thermal process.

A case study was presented and the experimental data and rate expressions obtained from the data were used to evaluate the design variables (i.e., pH, carbon dose, Cr(VI) concentration and mixing in the reaction vessel). Several Cr(VI) treatment schemes were proposed, together with an economic analysis of each scheme.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Adsorption Reduction Activated Carbon	Batch mode adsorption Packed Carbon Column Regeneration Hexavalent Chromium	13B

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