

**The Mechanisms for Free Chlorine Oxidation of Reduced
Manganese in Mixed-Media Filters**

by

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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Master of Science

in

Environmental Sciences and Engineering

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December, 1988
Blacksburg, Virginia

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(ABSTRACT)

The removal mechanisms of soluble manganese [Mn (II)] through mixed-media filters were investigated. Experimentation was directed toward the continuous supply of an oxidant during column filter studies. Free chlorine (HOCl, OCl⁻) was chosen to increase soluble manganese removal efficiency because chlorine is readily available and inexpensive.

Filter media from four different water treatment plants were used in this study. Continuous-flow filter columns were operated in the presence and absence of 2.0 milligrams per Liter (mg/L) free chlorine. Maintaining constant influent manganese concentrations of 1.0 mg/L and flow rates of 2.5 gallons per minute per foot squared (gpm/ft²), the operational pH values of 6-6.2, 7.8 and 8.8 were investigated.

Results indicate that a continuous feed of free chlorine (2 mg/L) applied to the filter columns could increase manganese (II) removal efficiency. However, the amount and oxidation state of the MnO_{x(s)} surface coating initially on the media and the influent pH had major influences upon the uptake of soluble manganese. From numerous Mn (II) uptake studies with different media and varying pH conditions, oxide-coated filter media continuously regenerated with free chlorine could result in increased soluble manganese

removal through adsorption upon the $\text{MnO}_{x(s)}$ surface coating and subsequent oxidation directly on the media surface. The relationships of manganese removal and chlorine consumed were also explored.

To further investigate the mechanisms of free chlorine oxidation for the removal of reduced manganese, pH 5.0 backtitrations were conducted following exhaustion of the filter media. The exposure of such low pH conditions to columns operated in the presence and absence of HOCl would ascertain if oxidation of the adsorbed Mn^{2+} was always occurring, regardless of an oxidant feed. Results indicated that in the absence of HOCl, the mechanisms for manganese removal on oxide-coated filter media were adsorption only. With the additional of HOCl, the adsorbed Mn^{2+} is oxidized directly on the surface of the media, thereby, continuously regenerating the surface oxide coating.

Additional work was begun to ascertain if free chlorine could be used as a viable alternative to potassium permanganate (KMnO_4) regeneration of oxide-coated filter media. Preliminary findings indicate from column cycling experiments that free chlorine could be used to regenerate oxide-coated filter media prior to backwashing.

Acknowledgements

The author wishes to thank the many people who aided, guided and shaped this document into its final product. In particular Dr. W. R. Knocke, Dr. Robert C. Hoehn and Dr. Gregory D. Boardman for serving on the advisory committee, the American Water Works Association for their financial support and last but not least, the many friends of 325 Norris. Although it is difficult to acknowledge each person individually, the friendships gained during my years in Blacksburg will be cherished for a long, long time.

A very special thanks to my good friends, _____ and
(a.k.a. Ram) for their much needed computer input, _____ for helping to pre-
pare for oral presentations, _____ for his research partnership, _____ for
not only her lab expertise but also as a fellow, casual tennis buff and
for analyzing samples on the new AA.

Acknowledgement must also go to my dear friend, _____ for his contin-
uous support and love throughout this masters, and finally the Virginia Tech Field
Hockey Club who gave me the outlet I needed to survive the past two and a half years.

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INTRODUCTION

Concern for problems associated with high manganese concentrations in public water supplies has increased steadily over the years. This is due to the fact that exceeding the recommended secondary maximum contaminant level of 0.05 mg/L for manganese will often cause aesthetic problems such as discoloration of water, staining of laundry and plumbing fixtures, and increased turbidity. Elevated manganese concentrations can also accelerate biological growths in the distribution systems, clogging pipelines and further contributing to taste, color and odor problems.

Higher concentrations of manganese are more prevalent in groundwaters and in the hypolimnetic region of lakes and reservoirs. Under anaerobic conditions, reduced Mn (II) is released into solution by biological activity. Water treatment plants typically remove this reduced manganese using an oxidation process followed by coagulation, sedimentation and/or filtration of the resulting precipitates. The most common oxidizing agents used by water utilities are oxygen, chlorine and potassium permanganate.

In aeration-filtration processes, oxygen from the atmosphere reacts with the manganese in raw water, producing insoluble manganic oxides. The rate of oxidation depends on

solution pH; at higher pH values ($> \text{pH } 9.5$) the reaction occurs fairly rapidly (1). Since manganese has such a slow oxidation rate via $\text{O}_{2(\text{aq})}$, this technique is not very effective for Mn (II) removal. Additional retention time and supplemental chemical treatment are often required to decrease manganese concentrations to the desired level.

Manganese (II) removal by the addition of chlorine has been used for many years because chlorine is readily available and inexpensive. However, the need to modify treatment practices to minimize the formation of organics has rendered chlorination an inefficient process for Mn (II) removal in certain facilities. Elimination of chlorine until just prior to filtration does not allow sufficient contact time for complete oxidation of soluble manganese; therefore, stronger oxidants are often employed. For example, potassium permanganate is effective in oxidizing soluble manganese; however, studies by Knocke *et al.* (2) have indicated that high TOC concentrations, low oxidation pH and/or low temperature conditions can adversely affect permanganate oxidation efficiency.

A few water utilities have replaced typical, dual-filter media of sand and anthracite coal with commercially produced manganese greensand. This particular filter media is a zeolite mineral impregnated with manganese oxide to promote the exchange of electrons and, thereby, oxidize the manganese to its insoluble and filterable state (1). Potassium permanganate is used in conjunction with this Mn greensand. This process has an advantage in that if the KMnO_4 does not completely oxidize all the soluble manganese, the greensand will allow for completion of the oxidation process. A major drawback to Mn greensand filtration is its limited oxidative capacity and the need for the bed to be regenerated with KMnO_4 .

Over the years, certain publications have reported on an apparent naturally-occurring "greensand effect". This phenomenon is observed when soluble manganese is removed by mixed-media filters in the absence of commercial Mn greensand. Knocke *et al.* (3) reported the "natural greensand effect" is due to a surface manganese oxide coating that develops on filter media over time. The removal efficiency of Mn (II) is a function of this surface manganese dioxide concentration, its oxidation state and the applied water pH. Furthermore, the addition of chlorine prior to filters resulted in Mn (II) being directly oxidized on the media's oxide surface coating (3).

From the results of the documentation cited above, it was hypothesized that perhaps the presence of free chlorine upon the oxide-coated filter media would be an inexpensive and viable alternative to soluble manganese removal. To evaluate the above hypothesis, the following research objectives were proposed:

1. Characterize the Mn (II) removal potential of oxide-coated, water treatment plant filter media as a function of solution pH and media surface, oxide-coating concentration;
2. Gain a better understanding of the Mn (II) removal mechanisms by oxide-coated filter media in the presence and absence of free chlorine;
3. Determine if free chlorine can continually oxidize the oxide surface coating on the filter media during Mn (II) removal; and
4. Determine if free chlorine can be used as a viable alternative to KMnO_4 for the regeneration of oxide-coated filter media.

LITERATURE REVIEW

Water Quality Concerns for Manganese

In roughly 40% of the public water supply systems in the United States, soluble manganese concentrations exceed the secondary maximum contaminant level (SMCL) of 0.05 mg/L (4). This MCL was established primarily for aesthetic concerns, since the problems associated with elevated manganese concentrations include staining of laundry and plumbing fixtures, discoloration of water and taste and odor problems. The growth of manganese-induced microorganisms in the distribution system can also reduce the carrying capacity of pipelines and clog meters and valves (5). Despite these annoying problems experienced by consumers and industries, there have been no reported harmful effects from drinking waters containing elevated manganese concentrations.

Manganese is a common constituent of impounded surface waters and many well waters. The earth's crust consists of approximately 0.1% manganese distributed evenly throughout (6). Chemical and biological processes contribute to the occurrence of manganese in water. Chemical reactions account for the greater part of manganese in groundwater; in lakes and reservoirs, elevated Mn (II) concentrations often occur due to a combination of biologic and chemical processes working simultaneously (6). Within these

impounded waters, the problems of increased Mn (II) levels are often seasonal conditions occurring during the overturn of the lake or reservoir.

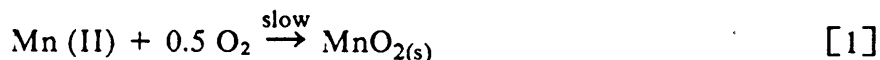
The occurrence of manganese problems in water supplies depends on the character of the source supply, the type of treatment and the usage of the finished water (domestic or industrial). The availability of information on the removal methods to be employed for a specific water supply is difficult to obtain. The demand for answers to questions concerning manganese removal is an indication that research is still needed to solve many of these manganese-related problems.

Chemistry of Manganese

To gain a better understanding of the control techniques available for Mn (II) removal in water supplies, the aqueous chemistry of manganese must first be explored. Manganese has eight oxidation states: (0) Mn, (II): Mn^{2+} , (2.67): $\text{Mn}_3\text{O}_4(\text{s})$, (III): $\text{Mn}_2\text{O}_3(\text{s})$, (IV): $\text{MnO}_2(\text{s})$, (V): MnO_4^{3-} , (VI): MnO_4^{2-} and (VII): MnO_4^- ; however, not all are relevant to the field of water treatment (5). Most utilities are concerned with manganese in the 2+, 4+ and 7+ oxidation states. Aqueous manganese in the Mn (II) valence state occupies a large portion of the pE-pH regime associated with natural waters (See Figure 1). The oxidation and control of manganese is complicated by factors that range from misunderstanding the reaction chemistry to slow kinetics and numerous oxidation states that result from the oxidation reaction. Manganese precipitates can also be affected by formation of organic complexes (8).

Reactions of Mn (II) with Oxygen

Morgan (9) has suggested the following sequence of reactions to describe Mn (II) oxidation by $\text{O}_{2(\text{aq})}$:



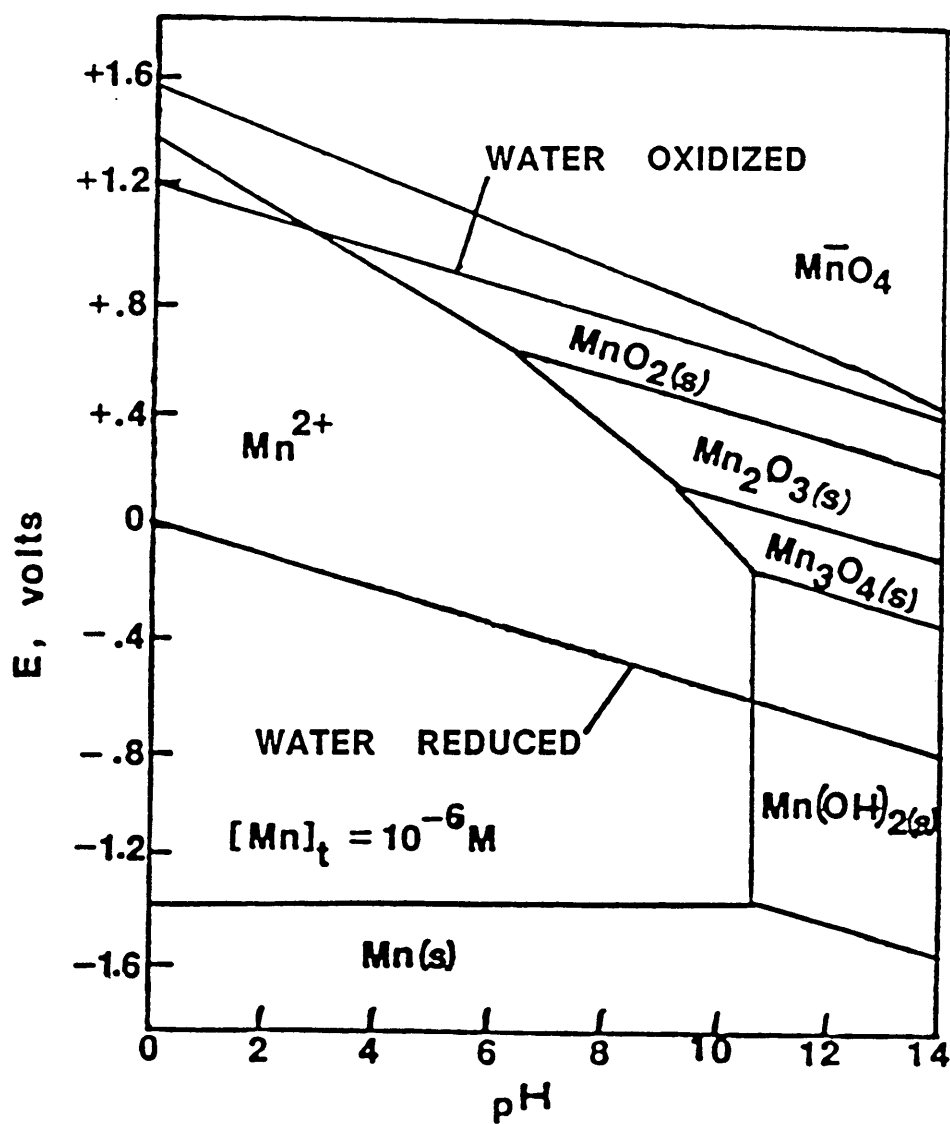
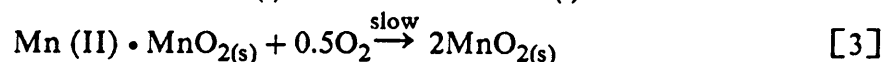
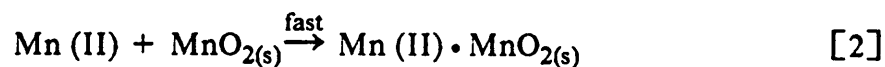


Figure 1. pE-pH Stability Diagram for Various Manganese Species in Water
[Temp = 25°C; from (7)]



Experimental data collected by Stumm and Morgan (10) showed the extent of observed Mn (II) removal from solutions containing $\text{O}_{2(aq)}$ did not follow the stoichiometry of equations 1-3, indicating an autocatalytic model. In slightly alkaline solutions, significant amounts of Mn (II) is adsorbed onto higher oxides of manganese. Since the solid phase from the oxygenation may range from $\text{MnO}_{1.3}$ to $\text{MnO}_{1.9}$ oxidation to MnO_2 is not complete (11).

The autocatalytic model proposed by Morgan (12) to describe overall removal in this system is:

$$\frac{-d[\text{Mn (II)}]}{dt} = k_1[\text{Mn (II)}] + k_2[\text{Mn (II)}][\text{MnO}_{2(s)}] \quad [4]$$

where k_1 and k_2 are oxidation and adsorption removal rate constants, respectively.

Reactions of Mn (II) with Alternative Oxidants

Since manganese reactions with oxygen are often slow and pH dependent, other oxidants are employed to effectively remove manganese. These include chlorine, potassium permanganate, chlorine dioxide and ozone. Table 1 shows the reactions of Mn (II) with alternative oxidants and the theoretical reaction stoichiometry.

1. Free Chlorine

The removal of Mn (II) by free chlorine has been reported in publication over forty years ago due to its availability and inexpensiveness. In 1946, Edwards and McCall (16) reported that breakpoint chlorination could effectively eliminate manganese problems, and the manganese coated sand in the filters was in part responsible for the complete

Table 1. Reactions of Mn (II) with Alternative Oxidants and the Theoretical Amounts of Oxidant to Oxidize 1.0 mg/L Mn (II)

REACTION	EQUATION NUMBER
$\text{Mn}^{2+} + \text{HOCl} + \text{H}_2\text{O} \rightleftharpoons \text{MnO}_{2(s)} + \text{Cl}^- + 3\text{H}^+$	[5]
$3\text{Mn}^{2+} + 2\text{MnO}_4^- + 2\text{H}_2\text{O} \rightleftharpoons 5\text{MnO}_{2(s)} + 4\text{H}^+$	[6]
$\text{Mn}^{2+} + 2\text{ClO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{MnO}_{2(s)} + 2\text{ClO}_2^- + 12\text{H}^+$	[7]
$\text{Mn}^{2+} + \text{O}_{3(aq)} + \text{H}_2\text{O} \rightleftharpoons \text{MnO}_{2(s)} + \text{O}_{2(aq)} + 2\text{H}^+$	[8]

Oxidant	Theoretical Stoichiometry
HOCl	1.30 mg HOCl/mg Mn
KMnO ₄	1.92 mg KMnO ₄ /mg Mn
ClO ₂	2.45 mg ClO ₂ /mg Mn
O ₃	0.88 mg O ₃ /mg Mn

manganese removal. In the following year, however, Mathews (17) noted the ability to remove Mn (II) by free residual chlorination without the necessity of a coating of manganese dioxide accumulated on the sand grains of the filter. In contrast, others have reported the importance of a "seasoning" or "aging" of the filter media but little information on the deposited MnO_2 on the sand grains was available at that time (6). Very recently, Knocke *et al.* (3) have directed their studies on the importance of the manganese dioxide coating on filter media as an efficient mechanism for Mn (II) removal. Weng (18) also reported that to remove manganese to an acceptable level, an autocatalytic reaction on the sand or anthracite media coated with manganese oxide must take place during filtration.

For many years it was common practice to control Mn (II) by the addition of chlorine under alkaline conditions. In recent years, water treatment facilities have directed their attention to the removal of organics. The reaction of chlorine with organic compounds results in the formation of trihalomethanes (THMs). Since these are potentially carcinogenic compounds, the USEPA has established a maximum level of 0.1 mg/L for THMs. In response to this THM regulation, many water treatment plants have modified prechlorination practices and have moved the point of chlorination to just prior to filtration. This drastically reduces the time available for Mn (II) oxidation by free chlorine.

Recently Knocke *et al.* (2) have studied new strategies for removing dissolved manganese while optimizing organics removal, and have concluded that manganese oxidation by free chlorine is severely inhibited at low temperatures and acidic pH conditions.

2. Potassium Permanganate

Although more expensive than chlorine, potassium permanganate has been used for Mn (II) removal and reduction of taste and odors. To help reduce chemical costs, KMnO_4 is often used in combination with chlorine. Unlike chlorine, the reaction of KMnO_4 with Mn (II) is rapid and complete at pH 5.5-9.0 (1, 2). Knocke *et al.* (2) showed that increased organic carbon concentrations required greater doses of KMnO_4 to accomplish Mn (II) oxidation. Results from this study also indicated a substantial decrease in Mn (II) oxidation efficiency under low temperature (5°C) conditions.

As with chlorine, the importance of the oxide coating on the media surface greatly influenced Mn (II) removal. Morgan and Stumm (19) showed that sorption of Mn (II) on MnO_2 is pH dependent (See Figure 2). Weng *et al.* (17) showed that when the sorption capacity of the manganese oxide coating on the media had been exhausted, the media could be regenerated with HOCl or KMnO_4 .

The use of KMnO_4 discussed in the previous paragraphs is for more conventional gravity systems used by large municipalities. However, KMnO_4 is also utilized in pressure systems in conjunction with manganese-treated greensand. This removal technique is discussed further in a subsequent section.

3. Chlorine Dioxide

Application of chlorine dioxide can be beneficial to water utilities due to its disinfectant capability, control of taste and odors, THM precursor reduction and soluble manganese removal (20-22). The aqueous chemistry of ClO_2 is somewhat more complicated than HOCl and KMnO_4 (23). In most water treatment plants, the conditions are such that ClO_2 reduces to chlorite (ClO_2^-) and the complete reduction to chloride (Cl^-) does not occur. The total sum of chlorine dioxide, chlorite and chloride concentrations must not

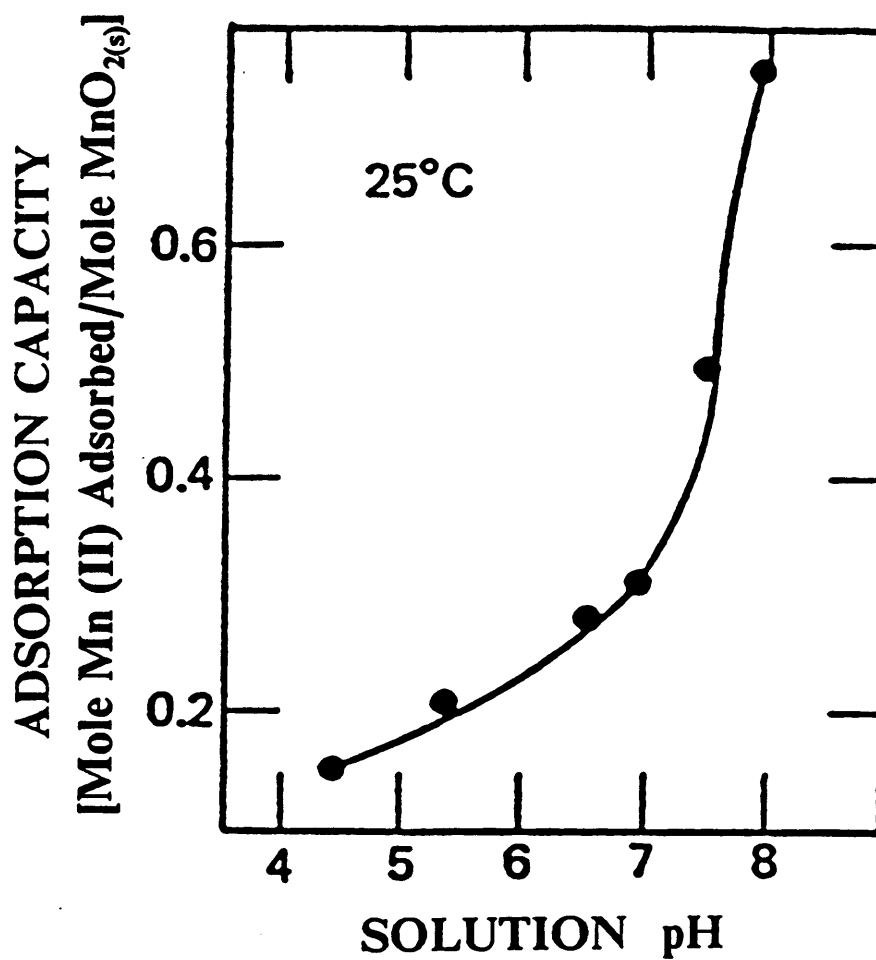


Figure 2. Influence of pH on the Sorption of Mn (II) on MnO₂ at 25°C
[from (19)]

exceed 1 mg/L in the finished water due to reported health concerns (24). This concern limits the ClO_2 dose that can be applied and may not be sufficient to meet the required oxidant demand of the raw water. It may be necessary to use ClO_2 in conjunction with other oxidants to control persistent Mn (II) problems (2, 20).

4. Ozone

A common oxidant used in Europe, ozone is gaining more attention within the U.S.. Ozonation can produce a finished water with improved taste and odor and less sludge production (18). An extremely strong oxidant, ozone is also used for disinfection, algal control and iron and manganese removal (20). Legube *et al.* (25) have shown the effects of ozonation on manganese removal by sand filtration in the presence of organics (See Figure 3). The required ozone dose to obtain effective manganese removal increases with larger residual TOC concentrations. The presence of humic substances lowers the efficiency of ozone in the removal of manganese. Major concerns that limit the use of ozone are the lack of residual after application and the costs associated with ozone generation (21).

Removal and Control Techniques

Ion Exchange

The method of ion exchange using a sodium resin or a hydrogen cation exchange material can be employed to remove Mn (II) from solution. This technique is limited to waters with low dissolved solids content because ions such as Mg^{2+} and Ca^{2+} will compete with the Mn (II) for sites on the exchange medium. Under certain conditions, this method is applicable and economical because the process can be almost completely automated except for periodic chemical cleaning of the ion exchange resin (26). One of the major difficulties involved in this control method is that if the Mn (II) is oxidized by dissolved oxygen in the water, the media will become coated and fouled (8). As a

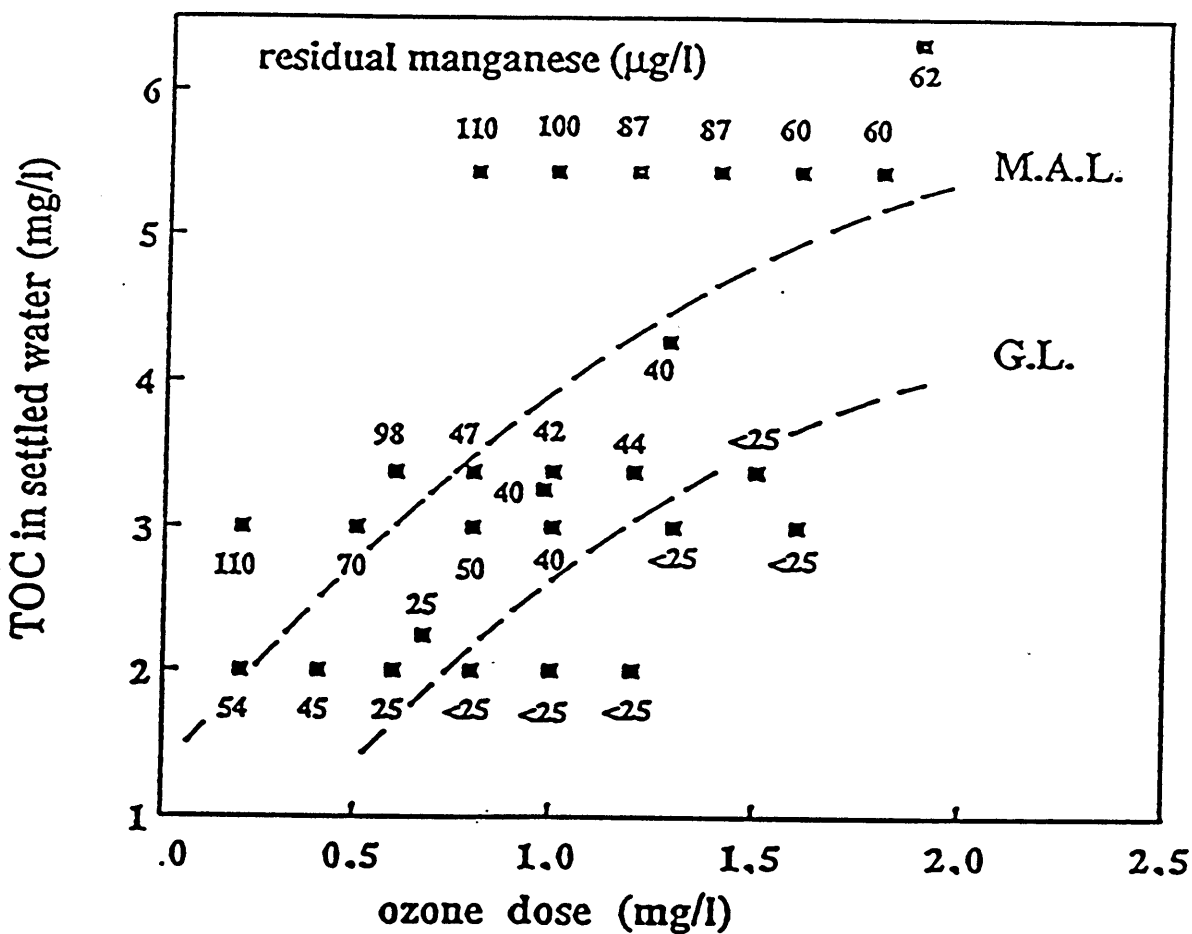


Figure 3. Ozonation Effects on Mn (II) Removal by Sand Filtration in the Presence of Organics: Following Coagulation, Sedimentation and Remineralization [Guide Levels (G.L.); Maximum Admissible Levels (M.A.L.) from (24)]

result, it is important to control the levels of dissolved oxygen in an ion exchange resin that is used to remove elevated Mn (II) levels.

Mn (II) Removal by Mn Greensand

Manganese greensand is a zeolite mineral processed with manganese sulfide and potassium permanganate in alternating steps to produce a black precipitate of manganese dioxide on the granules (27). The hydrous oxides of manganese deposited on the filter media have a large sorption capacity for Mn (II) (5). Morgan and Stumm (19) have shown the sorption of Mn (II) on MnO_2 is pH dependent (Refer to Figure 2). The greensand coated with MnO_2 is capable of exchanging electrons and thereby oxidizing the adsorbed Mn (II) to its filterable state (1). In essence, greensand acts as an adsorber of soluble manganese, an oxidizing contact medium and a filter medium (11). Drawbacks to this technique for Mn (II) removal are the limited oxidative capacity of the greensand and the exhausted media must be regenerated with KMnO_4 . A 1-4 % KMnO_4 solution may also be fed into the raw water line prior to filtration to reduce the amount of soluble manganese going to the filter (1). The expense of this chemical requirement contributes to its high operational costs; often, chlorine is used in conjunction with KMnO_4 to help control these costs.

The KMnO_4 regeneration oxidizes the lower oxides present on the media surface to higher oxides to restore the catalytic properties of the bed. These catalytic properties do not pertain to the actual greensand granules but is a property of the oxidized manganese present on the surface (27). This autocatalytic nature has been previously shown by Morgan (12) to be the $\text{O}_{2(\text{aq})}$ removal mechanism of Mn (II) from aqueous solution at pH of about 9.0. The autocatalytic properties are produced by the n-type, extrinsic, semi-conductive properties of the oxygen deficient manganese dioxide crystals formed and precipitated. The vacancies produced from insufficient oxygen increase the

conductivity of the quasi-free Mn electrons to the surface. These electrons on the surface promote the ionization of O_2 which is held to the manganese surface, thereby increasing the velocity of the Mn oxidation reaction. However, once the Mn surface has been oxidized to $MnO_{2(s)}$, no further autocatalytic oxidation will occur and regeneration is necessary. (28)

Manganese greensand is either continuously or intermittently regenerated with $KMnO_4$. Intermittent regeneration consists of backwashing, regeneration with 0.5-1% dilute solution of $KMnO_4$, and subsequent rinsing. This regeneration allows for longer filter runs at higher flow rates because head losses build up more slowly. Lower head losses are due to the fact that solid particulate manganese is not retained within the filter bed. Instead, manganese is being directly oxidized on the filter media which helps prevent clogging of the filter media. However, all the manganese removal takes place on the filter and the growth of the filter media must be accounted for in the design (29).

The oxidative capacity of the greensand is used more slowly in continuous regeneration because most of the manganese is oxidized before entering the filter. This reduces the amount of soluble manganese going to the filter. The greensand then acts as a "buffer" zone. If the $KMnO_4$ feed does not oxidize all the Mn (II), the excess manganese can be oxidized by the greensand. In contrast, if the $KMnO_4$ feed is in excess of the demand, it is used for regenerating the greensand. The Mn greensand is usually capped with anthracite coal to remove most of the precipitates so as not to bind the greensand (13) and thereby increase head loss. Backwashing is often utilized once sufficient head loss has built up. In continuous regeneration of Mn greensand, chlorine may be used in conjunction with $KMnO_4$ to reduce chemical costs.

Mn (II) Removal by Oxide-Coated Filter Media

As mentioned in the previous section, catalytic properties are associated with the oxidized manganese and not the actual zeolite material. In this section, the effective retention of Mn (II) by hydrous oxide coatings and subsequent oxidation by chlorine applied prior to the filters in the absence of Mn-treated greensand is discussed. Many water facilities employ dual-media filters of anthracite coal upon sand instead of the more costly Mn greensand.

Over the years, the removal of Mn (II) by the use of free residual chlorination has been documented. For example Edwards and McCall (16) reported in 1946 that a catalytic effect of the manganese-coated sand in the filters was responsible in part for Mn (II) removal. They also noted that chlorine dosages beyond the breakpoint could eliminate manganese problems in the filter effluent. Data presented in Figure 4 show the relationship of chlorine applied, residual chlorine and effectiveness of Mn (II) oxidation from their study.

In 1986, Weng *et al.* (18) noted the importance of an old or aged media coated with manganese oxide for efficient Mn (II) removal. However, the removal mechanisms by the "aging" or "seasoning" (6) of the filter media were not well documented until recent publications. Morgan and Stumm (19) had initially showed the significance of Mn (II) removal by sorption on $\text{MnO}_{2(s)}$, but experiences within water treatment filters were occurring without being recognized. Although black "coatings" were often reported on the sand grains in filters, it was not until recently that Knocke *et al.* (3) studied this "natural greensand" phenomenon. This "naturally-occurring greensand effect" involves the removal of soluble manganese across mixed-media filters in the absence of a commercial zeolite material and is a viable, functional treatment mechanism aiding Mn

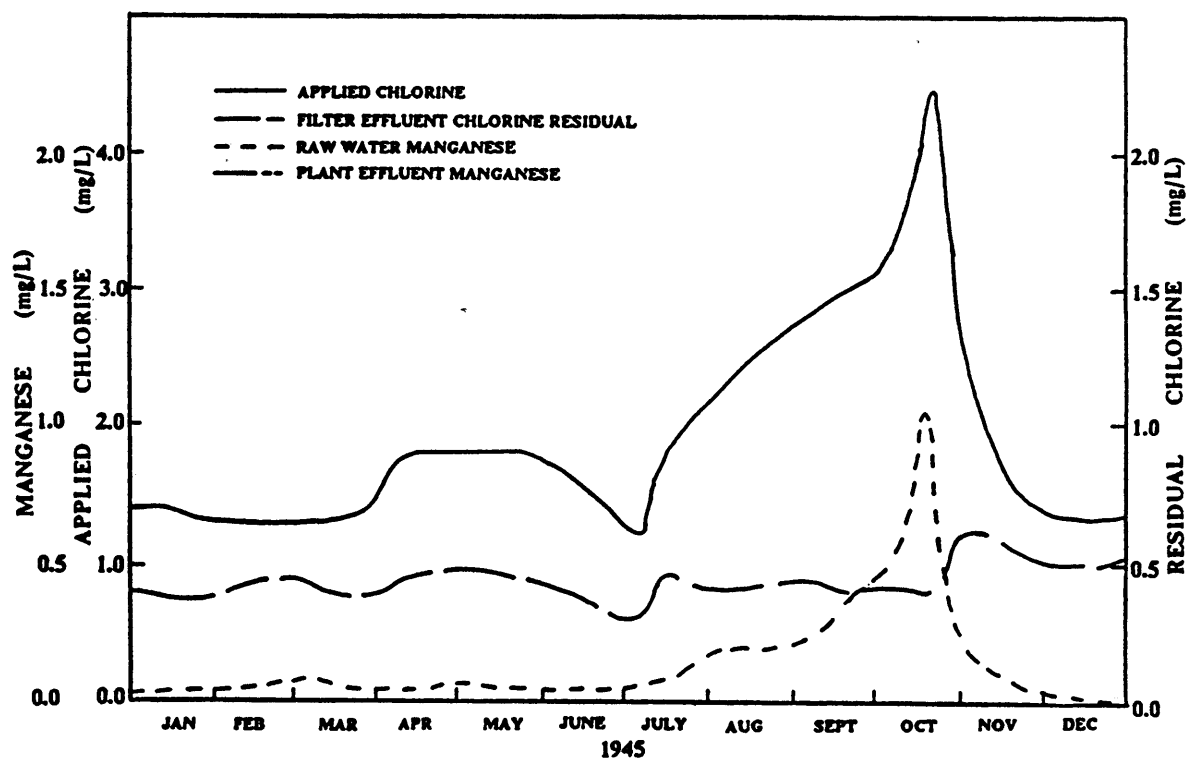


Figure 4. Relationship of Chlorine Applied, Residual Chlorine and Effectiveness of Mn (II) Oxidation and Removal: [Note: The dash and two-dot line (effluent manganese content) lies on the zero line and is obscure on the graph; adapted from Edwards & McCall from (16)]

removal operations. The removal efficiency is a direct function of the surface $\text{MnO}_{x(s)}$ concentration, its oxidation state and the applied water pH. Filter media with larger amounts of surface oxide-coating typically yielded efficient removal of manganese for longer periods of operation. Highly oxidized forms ($\text{MnO}_{1.8(s)} - \text{MnO}_{2(s)}$) of the oxide coating had an increased, soluble manganese removability. Acidic pH conditions effectively negate this removal mechanism (see Figure 5). The authors also reported on the addition of chlorine just prior to the filters resulted in Mn (II) oxidation directly on the oxide surface coating of the media, a reaction which is highly efficient at pH 6.0 or above. In the presence of significant free chlorine ($> 1\text{-}2 \text{ mg/L as Cl}_2$), soluble manganese uptake within oxide-coated filters will be rapid (see Figure 6).

Stabilization

An alternative to removal of manganese is to sequester soluble manganese with polyphosphates. Polyphosphates can be implemented quickly and economically to control the soluble manganese (8). O'Connor (5) reported this treatment will stabilize manganese in suspension but is not suitable for metal concentrations in excess of 1 mg/L. He also showed that higher water temperatures, causes the polyphosphates to revert to orthophosphates and lose this dispersing property. With mixed reactions from various water suppliers, this process is limited to polyphosphate dosages of 10 mg/L since the availability of phosphorous may stimulate bacterial growths in the distribution systems. If this occurs, chlorine residuals must be sufficient to control these bacterial slime growths (5).

In summary, it is apparent that no single treatment chemical nor treatment process will solve all reduced manganese problems. Because every water type has its own characteristics, on-site studies are recommended to develop the most reliable and cost effective method for manganese removal. Each treatment facility should determine which

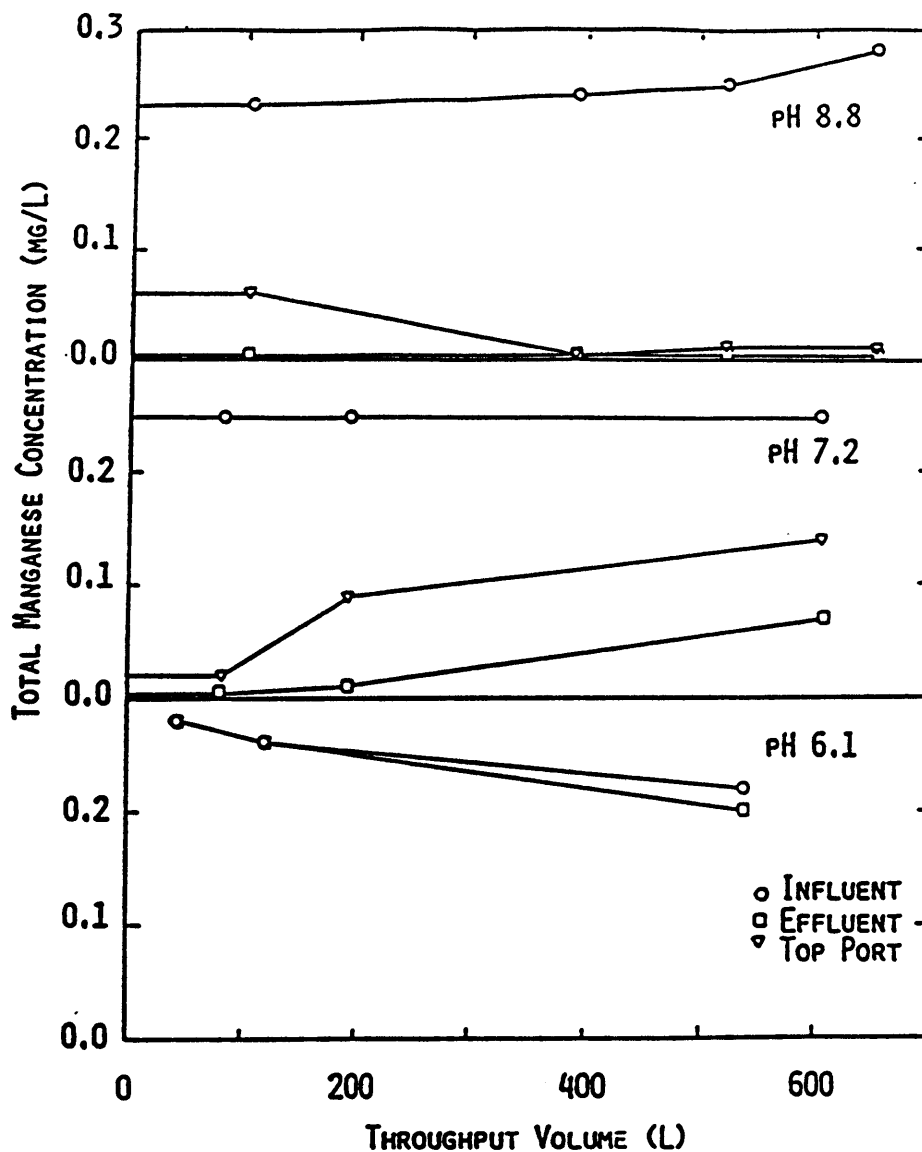


Figure 5. Effect of pH upon Mn (II) Removal by Oxide-Coated Filter Media in the Absence of an Oxidant [from (3)]

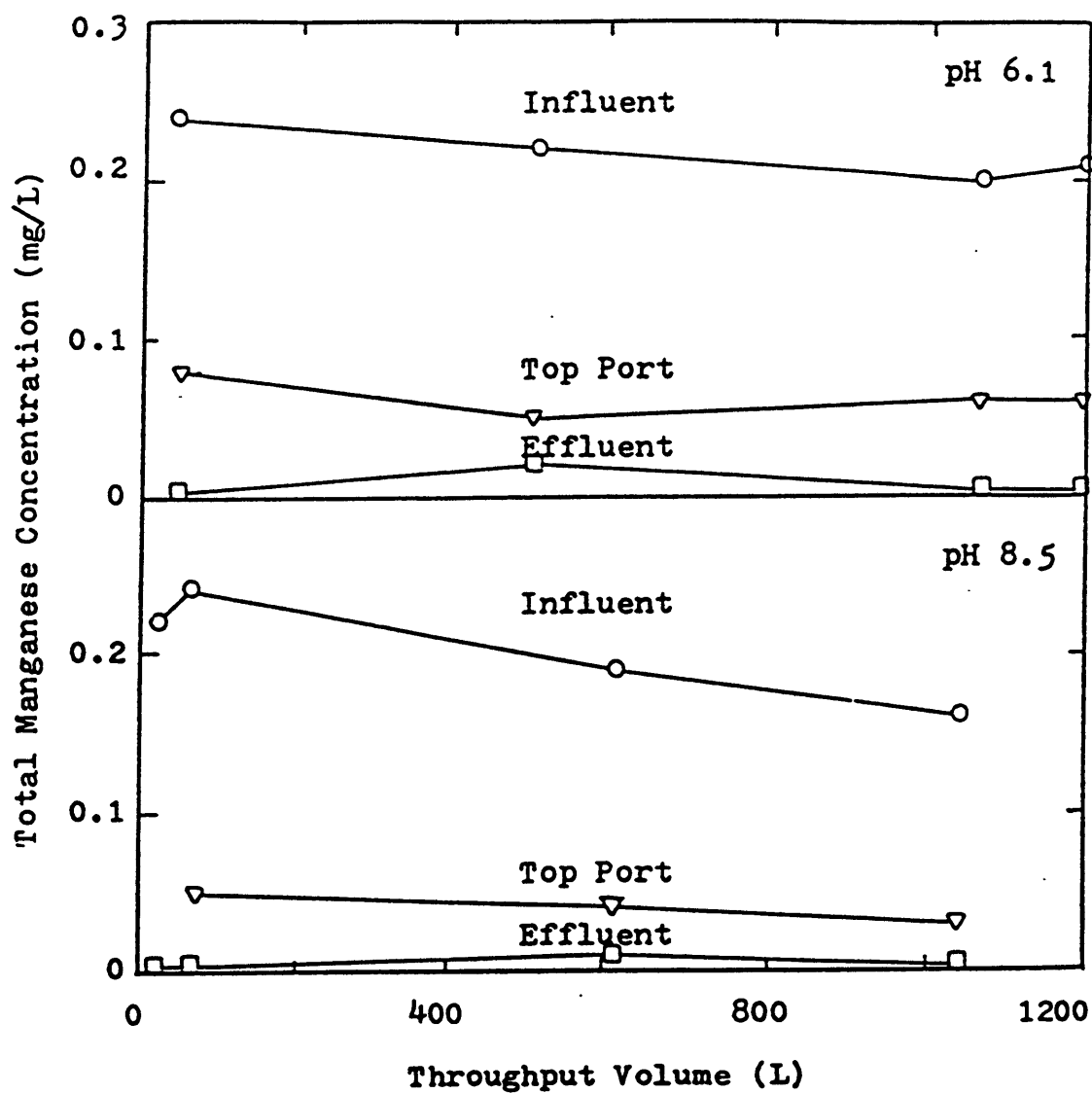


Figure 6. Effect of Solution pH and Free Chlorine Addition on Mn (II) Removal by Oxide-Coated Media [from (3)]

oxidants will promote effective manganese oxidation under their specific operating conditions.

METHODS AND MATERIALS

Experimental Design

Continuous-flow, laboratory scale filtration experiments were conducted using a four column apparatus (see Figure 7). Each 1 ft. long, 3/4 in. inner diameter column had an upper influent port and a lower effluent port; the distance between ports was approximately 10 inches. Two large, 35-gallon holding tanks were used for the influent manganese feed solution. A Cole-Palmer Masterflex pump was used to pump the manganese-containing feed water to an elevated constant head tank. The elevated tank was used to insure a consistent flowrate to the columns. A separate 50 L carboy was used for the chlorine feed solution which was pumped into the manganese-feed line with a Cole-Palmer diaphragm pump.

The configuration of the filter media within each column consisted of an inch of base gravel topped with 50 g of filter media from various water treatment plants in Virginia and North Carolina. Dual-media samples of anthracite coal and sand from four different treatment plants were used in the experiments. Unlike the typical 2 ft. configuration of dual-media filters with 2 distinct layers of coal and sand, the columns contained a mixture of the coal and sand ranging from 5 to 7.5 inches in depth. Such shallow media

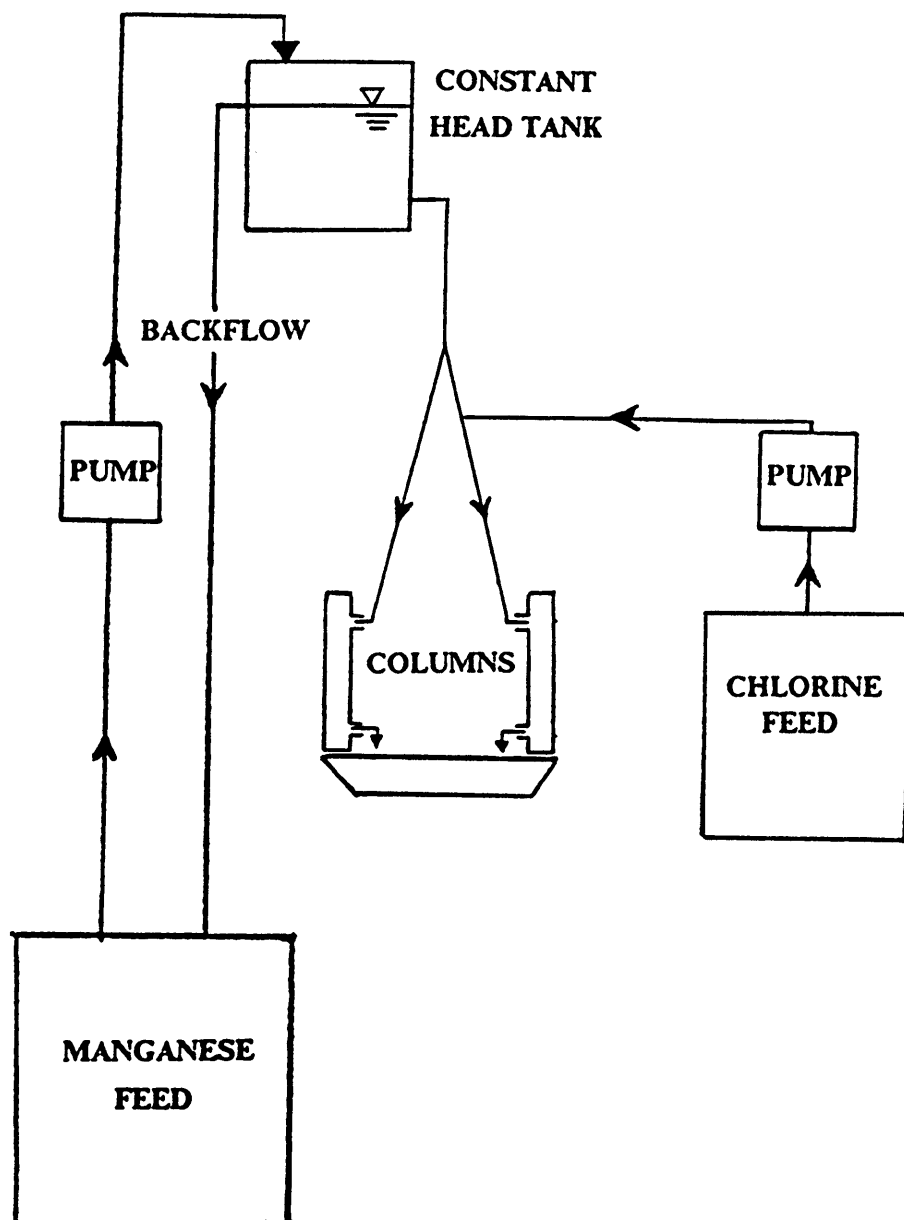


Figure 7. Experimental continuous-flow column apparatus

depths were used because a 24 inch column would have taken weeks to exhaust with respect to Mn^{2+} capacity. Failure of the filter media results in elevated manganese concentrations within the effluent. This study investigated 4 different media with varying amounts of manganese oxide coatings on the surface of the coal and sand. Duplicate tests were conducted with 2 columns receiving the 2 mg/L HOCl feed and 2 columns without the oxidant present (See Figure 8). A downflow filtration scheme of the manganese-treated tap water was typically operated at flowrates of 2.5 gpm/ft².

Laboratory Procedures

Preparation of Stock Solutions and Reagents

The main source of feed water to the columns was dechlorinated Blacksburg tap water augmented by various chemical additions. In preparing the soluble manganese feed solution, the tap water was first dechlorinated using 0.028 N sodium thiosulfate solution to prevent oxidation of the added manganese. Chlorine measurements were made using a Wallace & Tiernan amperometric titrator following the techniques outlined in *Standard Methods* (31). The 1.0 mg/L Mn (II) solution was prepared from a stock solution of manganous sulfate. An 8 mg/mL stock solution of manganous sulfate was prepared by adding 6.15 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ to 250 mL of distilled water. The pH of this solution was adjusted using appropriate amounts of concentrated HNO_3 and/or NaOH . A Fisher Accumet pH Model Meter was used to monitor influent and effluent pH values. Manganese concentrations were determined using a Perkin-Elmer Atomic Absorption Spectrophotometer.

A stock solution of free chlorine was made by 1:1 dilution of a 5.25% by weight solution of NaOCl with distilled water. A concentrated chlorine feed solution (14 mg/L) was generated from this stock solution and subsequently diluted to 2 mg/L when mixed with

the Mn (II) feed solution. The pump rate for the chlorine feed was adjusted accordingly to assure that a proper dilution was being made. Influent and effluent chlorine concentrations were measured using the amperometric titrator [refer to *Standard Methods* (30)]. The pH of this solution was also monitored and adjusted if necessary.

Characterizing Water Treatment Filter Media

A 2% by weight solution of KMnO_4 was used to regenerate four different media. Following preparation of the KMnO_4 , this solution was fed in an upflow manner through a column packed with media directly from packages sent from the water treatment plants. To insure the surface coating was completely oxidized, the permanganate regeneration was conducted until the effluent was similar in color to the influent. The KMnO_4 regeneration took approximately 1 hour after which the column was rinsed with distilled water until the effluent was clear. The media was then air dried for 24 hours before being packed into the columns.

To determine the total amount of manganese initially on the filter media surface following KMnO_4 regeneration, an extraction was performed. A strong reducing agent, hydroxyl amine sulfate (HAS), was used to reduce all the manganese to its most soluble oxidation state, Mn^{2+} .

Procedures for HAS Extraction

A 4 gram media sample was placed into a 250 mL Erlenmeyer flask. To provide the necessary acidic conditions, 100 mL of 0.5% HNO_3 was added prior to the addition of an excess amount of HAS (approximately 1 g HAS). After being covered with parafilm, the flasks were shaken and allowed to react for about 4 hours. This allowed for the manganese on the surface of the filter media to be solublized and, thereby, able to be analyzed on the Atomic Absorption Spectrophotometer (AA). Prior to analysis on the

on the AA, 10 mL of the extracted liquid were filtered through a 0.2 μm (25mm) Gelman membrane filter in order to remove any particulate matter.

The amount of total manganese on the media surface was determined using the following equation:

$$\frac{\text{Mn on surface}}{\text{unit mass media}} = \frac{(\text{d.f.})(V)(\text{conc.})}{\text{sample mass}} \quad [9]$$

where:

d.f. = dilution factor for AA analysis

V = volume of acid added to flask (i.e. 100 mL)

conc. = Mn conc. in acid solution after HAS addition

Manganese Removal Studies by Oxide-Coated Filter Media

To ascertain if a continuous oxidant supply would have an increased Mn removal capacity, two of the four columns were exposed to 2 mg/L free chlorine. All four columns contained the same amount and type of media. By operating duplicate columns, data on the reproducibility of the column tests could be achieved. Different experimental column tests were conducted at three different pH values (6.0-6.2, 7.8 and 8.8) using four different media samples. The continuous-flow columns were operated until the columns without chlorine failed or until five days had elapsed. Initially, frequent samples for effluent manganese and chlorine concentrations were collected. However, after the first day, samples were collected 3-4 times daily. All manganese samples were first filtered through 0.2 μm Gelman membrane filter to remove any particulate matter before AA analysis. Influent Mn and HOCl concentrations were periodically measured to insure the correct amounts were being fed through the columns. Flowrates were also monitored for each of the columns.

Column studies were continued until effluent manganese concentrations of columns without the HOCl present were 95% of the 1.0 mg/L Mn (II) influent. This amount is referred to as "exhaustion" of the media whereas the term "breakthrough" denotes the effluent concentration as being equal to 5% of the influent. Following exhaustion of the filter media without HOCl, all column flow was stopped and the amount of total Mn (II) uptake calculated. The calculation of Mn (II) uptake was determined by plotting effluent manganese concentrations versus volume of water treated (refer to Figure 8). The area between the effluent Mn curve and the influent 1.0 mg/L Mn (II) represents the total amount of Mn (II) uptake. A fortran program utilizing the trapezoidal method for determining areas above and below curves was executed for estimating these areas. The Mn (II) uptake was then expressed in milliequivalents for easier comparison with other data.

Potassium Permanganate Demands of Oxide-Coated Filter Media

After column operations ceased for Mn (II) removal, KMnO_4 demands on oxide-coated filter media were conducted on columns with and without the HOCl feed to evaluate the oxidation state of the $\text{MnO}_{x(s)}$ coating. A 100 mg/L KMnO_4 solution was fed in an upflow manner through the exhausted media. The KMnO_4 demand was the amount of oxidant (KMnO_4) required to oxidize the sorbed Mn^{2+} and is calculated similarly to the Mn (II) uptake. Effluent KMnO_4 concentration versus volume data were plotted and the area between the influent and effluent KMnO_4 concentration lines were estimated to represent the amount of KMnO_4 demand (see Figure 9). The amount of Mn (II) taken up, expressed in meq, should be theoretically equal to the demand for KMnO_4 . The oxidation state of the surface coating can be quantified by relating the KMnO_4 demand to the amount of Mn (II) taken up on the surface. KMnO_4 concentrations were determined using the Wallace & Tiernan amperometric titrator. The following equation

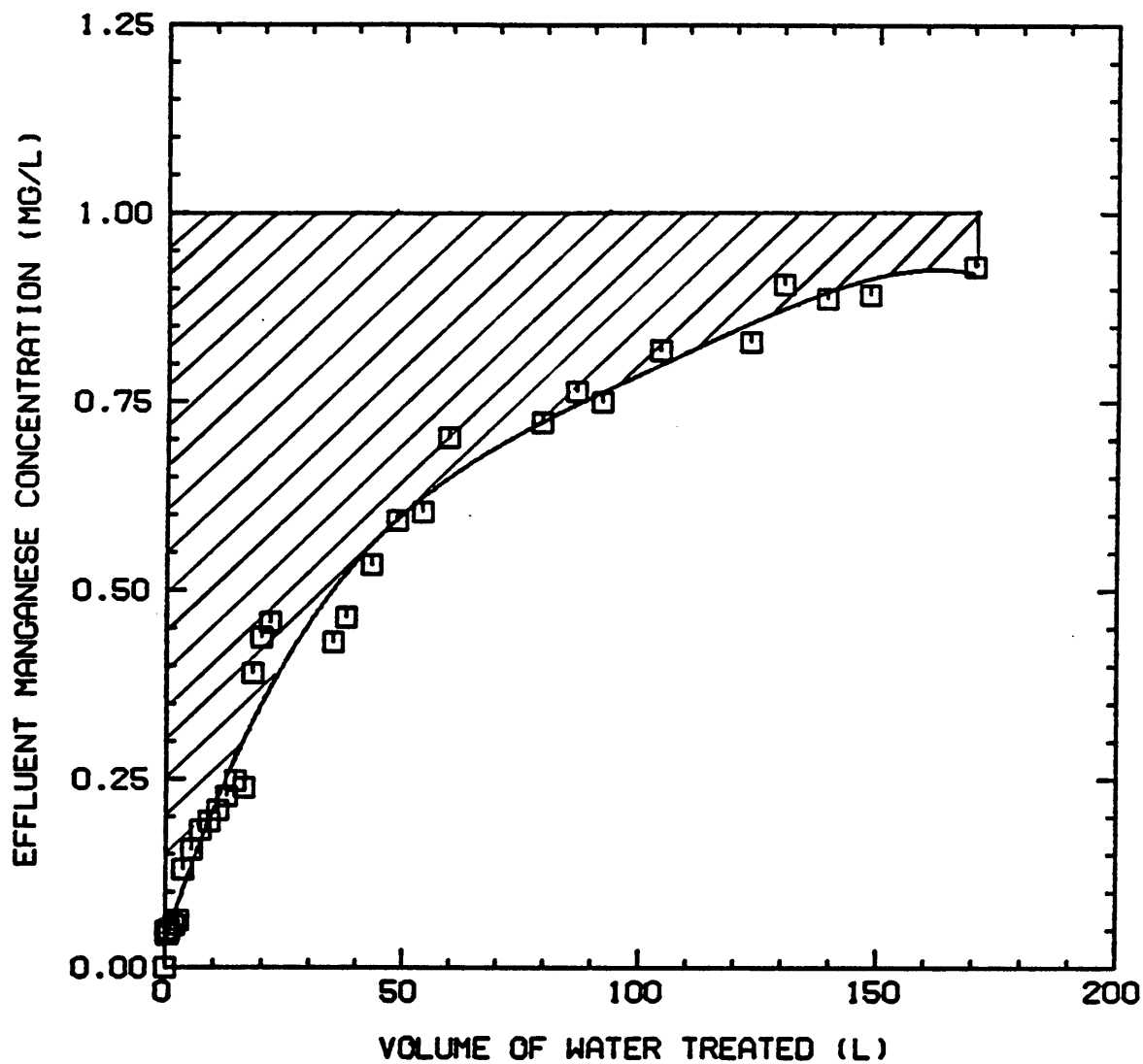


Figure 8. Mn (II) Uptake in the Absence of 2 mg/L Free Chlorine for Media #3 at pH 6-6.2 (Influent Mn (II) = 1.0 mg/L)

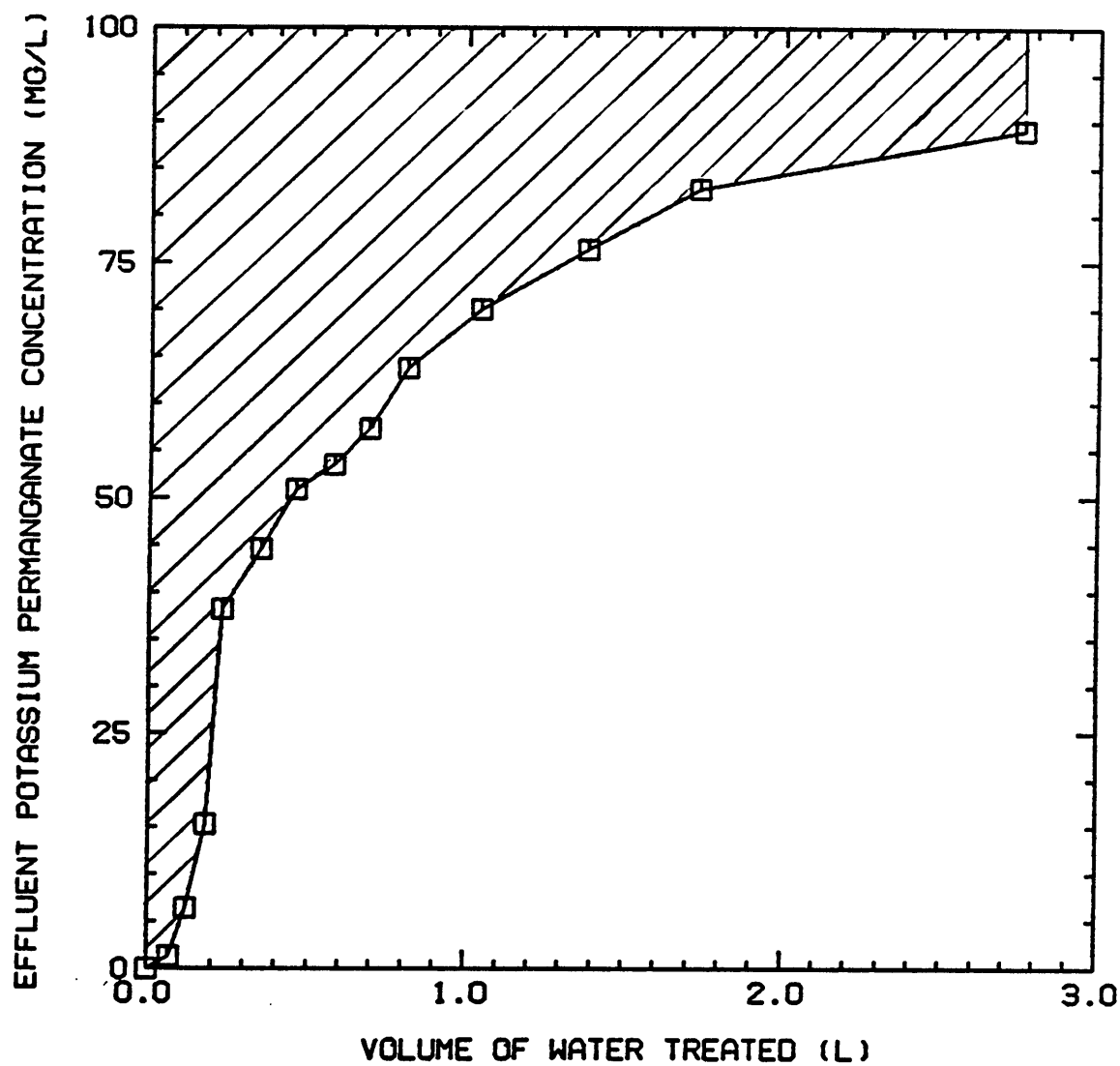


Figure 9. KMnO_4 Demand Performed on Exhausted, Oxide-Coated Filter Media

was used to calculate the concentration of KMnO_4 present from the amount of titrant required (20).

$$M = \frac{N V_1}{v V_2} \quad [10]$$

or

$$C = \frac{N V_1 G}{v V_2} \quad [11]$$

where:

M = molarity of permanganate solution

C = conc. of permanganate solution (mg/L as KMnO_4)

N = normality of titrant (eq/L)

G = gram molecular weight of KMnO_4 (158×10^3 mg/mole)

V_1 = volume of titrant (L)

v = electron equivalents transferred per mole of KMnO_4 (3.5)

V_2 = volume of sample (L)

Samples for effluent KMnO_4 determination were first filtered through Gelman 0.2 μm filters to remove any particulates. A 200 mL volume of distilled water was added to the filtered, effluent KMnO_4 sample (2 mL). The proper reagents (KI and pH 7 buffer) were added and the sample titrated using phenylarsine oxide (PAO).

Release of Mn^{2+} from Oxide-Coated Filter Media

In order to further investigate the mechanisms of Mn^{2+} uptake, filter columns were backtitrated with a pH 5.0 acid solution free of chlorine and manganese following the exhaustion of the columns without HOCl. This pH adjustment would help to clarify if an oxidation process of the adsorbed Mn (II) was occurring on the oxide surface both in the presence and absence of free chlorine. The pH 5.0 backtitration was used because at this pH value the Mn^{2+} species can be extracted without solubilizing the $\text{MnO}_{x(s)}$

coating (refer to Figure 1). Appropriate amounts of 10% HNO_3 were added to dechlorinated Blacksburg tap water to achieve a solution pH of 5.0, which was fed in a downflow manner at flowrates of 2.5 gpm/ft². The amount of soluble Mn in this water was less than 0.03 mg/L. Effluent Mn (II) concentrations and pH values were monitored. Effluent Mn (II) concentrations versus volume data were plotted and the area under this curve was estimated to represent the amount of sorbed Mn^{2+} released from the $\text{MnO}_{x(s)}$ coating. These experiments were conducted for 2-3 days to determine if the sorbed Mn in the the absence of HOCl would be released back into solution due to the fact that an oxidation process was not occurring. This would theoretically be accompanied by a rise in pH due to the protonation of the oxide surface coating. In contrast, columns operated with HOCl should not exhibit a release effect upon the addition of pH 5.0 solution due to oxidation of sorbed Mn^{2+} .

Repeated Mn^{2+} Uptake Studies with KMnO_4 and HOCl Regeneration

This particular study area was conducted to investigate the regeneration capabilities of KMnO_4 and HOCl of exhausted, oxide-coated filter media. These tests would determine if it was possible to recover all the removal capacity of the oxide coating by KMnO_4 addition during backwashing. An Mn (II) uptake study in the absence of HOCl was conducted on media #2 at pH 7.8. The influent Mn (II) concentrations were maintained at 1.0 mg/L with flowrates of 2.5 gpm/ft². Due to decreased availability of sorption sites upon the $\text{MnO}_{x(s)}$ coating, media #1 becomes exhausted. A 100 mg/L KMnO_4 solution was fed in an upflow manner to oxidize the adsorbed Mn^{2+} , thereby, contributing to the $\text{MnO}_{x(s)}$ coating. The amount of Mn (II) taken up and the KMnO_4 demand of the oxide coating was calculated as previously shown. Once the Mn^{2+} 's demand for KMnO_4 had been met, a second Mn (II) uptake study was performed using the same initial parameters (i.e. influent Mn (II) concentration, pH and flowrate). The amount of Mn (II) was again calculated and a final KMnO_4 demand of the oxide-coated filter

media was performed. The amount of KMnO_4 taken up was again calculated. The objective of this study was to evaluate the possibility of recovering the removal capacity of the oxide coating by KMnO_4 addition following exhaustion of the filter media.

One final experiment was to ascertain if free chlorine could be used as a viable alternative to using KMnO_4 to regenerate the surface coating during backwashing. Since KMnO_4 is a more costly oxidant, the cycling studies using HOCl were conducted to investigate the possible potential of its use for regeneration of the oxide coating during backwashing of the filters. Media #1 was again used in this study with the operational pH maintained at 7.8. Following the media's exhaustion, a 50 mg/L free chlorine (expressed as Cl_2) solution was fed at 15 mL/min in an upflow manner until the sorbed Mn^{2+} was oxidized. The Mn (II) taken up and the amount of HOCl used were calculated. Calculations made for determining HOCl demand were similar to those for KMnO_4 demands. Effluent HOCl concentrations versus volume were plotted and the area between the influent and effluent HOCl concentrations were estimated to represent the amount of HOCl demand. Once the HOCl demand for the adsorbed Mn^{2+} was completed, a second Mn (II) uptake study was performed. The amount of Mn (II) and subsequent HOCl taken up were calculated again. A third Mn (II) uptake test was conducted followed by a third and final HOCl regeneration of the oxide-coated filter media. Regeneration in this case is referred to the oxidation of only the adsorbed Mn^{2+} upon the $\text{MnO}_{x(s)}$ coating on media surface. By conducting these studies, the possibility of employing an inexpensive oxidant, free chlorine, for regeneration of oxide-coated filter media during backwashing operations would be ascertained.

RESULTS

In the following section, experimental results from continuous-flow laboratory filter columns are reported. These results are summarized into four subsections which include Mn (II) removal studies, potassium permanganate demands of oxide-coated filter media, release of Mn^{2+} from the oxide coating and repeated Mn^{2+} uptake studies with KMnO_4 and HOCl regeneration of exhausted media. These subsections are further divided into various subheadings to present the data in a lucid and concise manner.

Mn (II) Removal Studies

Most of the research emphasis was placed on this area of experimentation. Columns were operated in the absence and presence of free chlorine. Free chlorine was the oxidant employed in all studies because it is readily available and inexpensive. The effects of varying media and influent pH were extensively investigated. This particular subsection of Mn (II) uptake is further divided into the following subheadings: characterization of the filter media; column testing in the absence of chlorine; combined data of column studies with and without chlorine; and column studies in the presence of chlorine. Within the last subheading listed above, chlorine and manganese interactions are described through the presentation of combined plots of effluent Mn (II) and chlorine residual data.

Characterization of Water Treatment Plant Filter Media

Following a 2% KMnO_4 regeneration to fully oxidize the media surface coating, a hydroxyl amine sulfate (HAS) extraction was performed. These results are reported in Table 2. The total amount of manganese extracted per gram of media is listed for each of the different media investigated. Extracted iron concentrations are also shown since Morgan showed that ferric oxide solids also have a limited affinity for Mn^{2+} uptake (32). The data by Morgan (19) presented in Figure 10 show the pH effects on Mn (II) sorption by $\text{Fe}(\text{OH})_3$. Also presented in Table 2 are water treatment plant (W.T.P.) locations which supplied media and the media depths corresponding to 50 g of media within each column. Note that unlike typical water treatment plant filter depths of 12-24 inches, the height of media within the columns was much less.

Column Experiments in the Absence of Free Chlorine

Effects of Surface Oxide Concentration on Adsorption Capacity at Constant pH

Unless otherwise noted, all data presented in figures describe effluent manganese concentration (in mg/L) patterns as a function of the volume of water filtered through the column, (expressed in liters). Influent Mn^{2+} concentrations were maintained at 1.0 mg/L in all studies.

Data presented in Figure 11 indicate the importance of characterizing the media surface for the amount of oxide coating present. This particular figure shows the manganese uptake capacity of four different media at pH 6.0-6.2. Media having 3-4 mg/g of surface oxide coating show similar breakthrough curves. However, sample media #4 (42 mg/g of oxide coating) indicates a greater Mn^{2+} uptake capacity in the absence of free chlorine at pH 6-6.2. Subsequent studies for pH 7.8 and 8.8 conditions are reported in Figures 12 and 13, respectively. Again the figures indicate a greater capacity for uptake with increasing amounts of surface oxide coating. It is also evident that solution pH

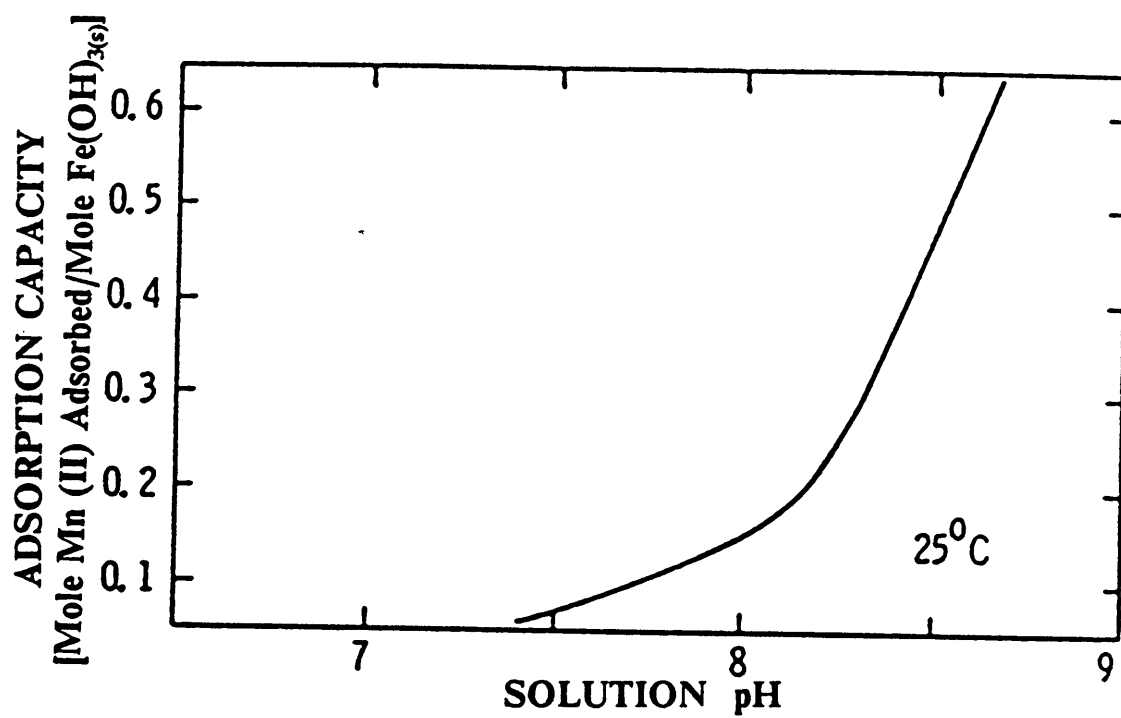


Figure 10. Mn (II) Sorption by Fe(OH)₃ as a function of pH [from Morgan (19)]

Table 2. Amount of Extracted Manganese and Iron Present on Filter Media Surface after 2% KMnO_4 Regeneration

MEDIA SAMPLE #	LOCATION OF W.T.P.	Mn CONC. (mg/g)	Fe CONC. (mg/g)	MEDIA DEPTH (in)
1	Cheasapeake Va.	3.0	3.0	6.5
2	Roanoake Va.	4.0	2.5	5
3	Newport News, Va.	14	4.2	6.5
4	Durham N.C.	42	---	7.5

also has an important role in defining the manganese removal capacity of oxide-coated filter media.

Effects of pH on Adsorption Capacity for Oxide-Coated Filter Media

The Mn (II) uptake of the four different water treatment plant filter media was highly dependent upon the pH of the influent water. Data presented in Figures 14-17 show the effect pH had upon manganese removal efficiency. Uptake was severely impeded at pH values of 6-6.2; greater capacities for removal were observed as solution pH increased. The results of the particular media containing 3-4 mg/g of surface oxide coating are presented in Figures 14 and 15. In contrast, Figures 15 and 16 indicate observed manganese removal capacity for the filter media samples which had larger amounts of surface oxide coating.

Data from Figures 14-17 are summarized in Table 3 to show the total amount of soluble manganese removal for each media at the three pH values investigated. Note that the removal amount is expressed in total manganese milliequivalents (meq).

Column Studies in the Absence and Presence of Free Chlorine

In operating a four column apparatus, two columns could be exposed to 2.0 mg/L free chlorine. Two different media could therefore be studied, one column receiving the HOCl feed and the other column operated in the absence of the oxidant. The data presented in this section indicate a continuous feed of an oxidant could enhance Mn (II) removal (see Figures 18-21). These figures show overlay plots of simultaneous tests with and without chlorine. The effect of pH upon a media (media #2) with a less amount of oxide coating (4 mg/g) is shown in Figures 18-20. Media #3 which has a larger amount of oxide coating (14 mg/g) is presented in Figure 21. Table 4 follows these figures and summarizes the data collected during these experimentations.

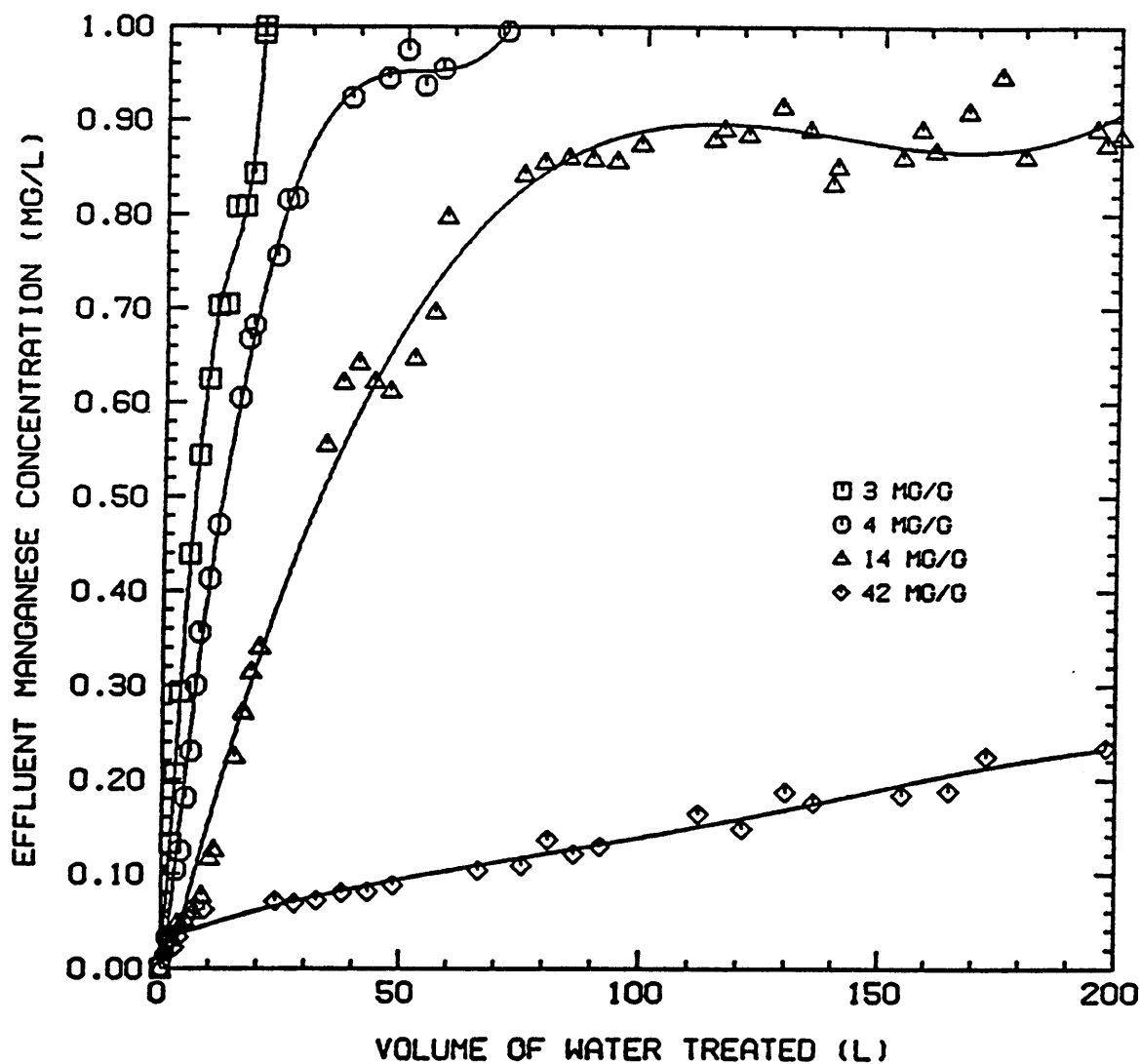


Figure 11. Effect of Surface Oxide Concentration on Mn (II) Uptake by Different Media at pH 6-6.2: [Influent Mn (II)= 1.0 mg/L; no HOCl in filter applied water; symbols denote surface extracted concentration]

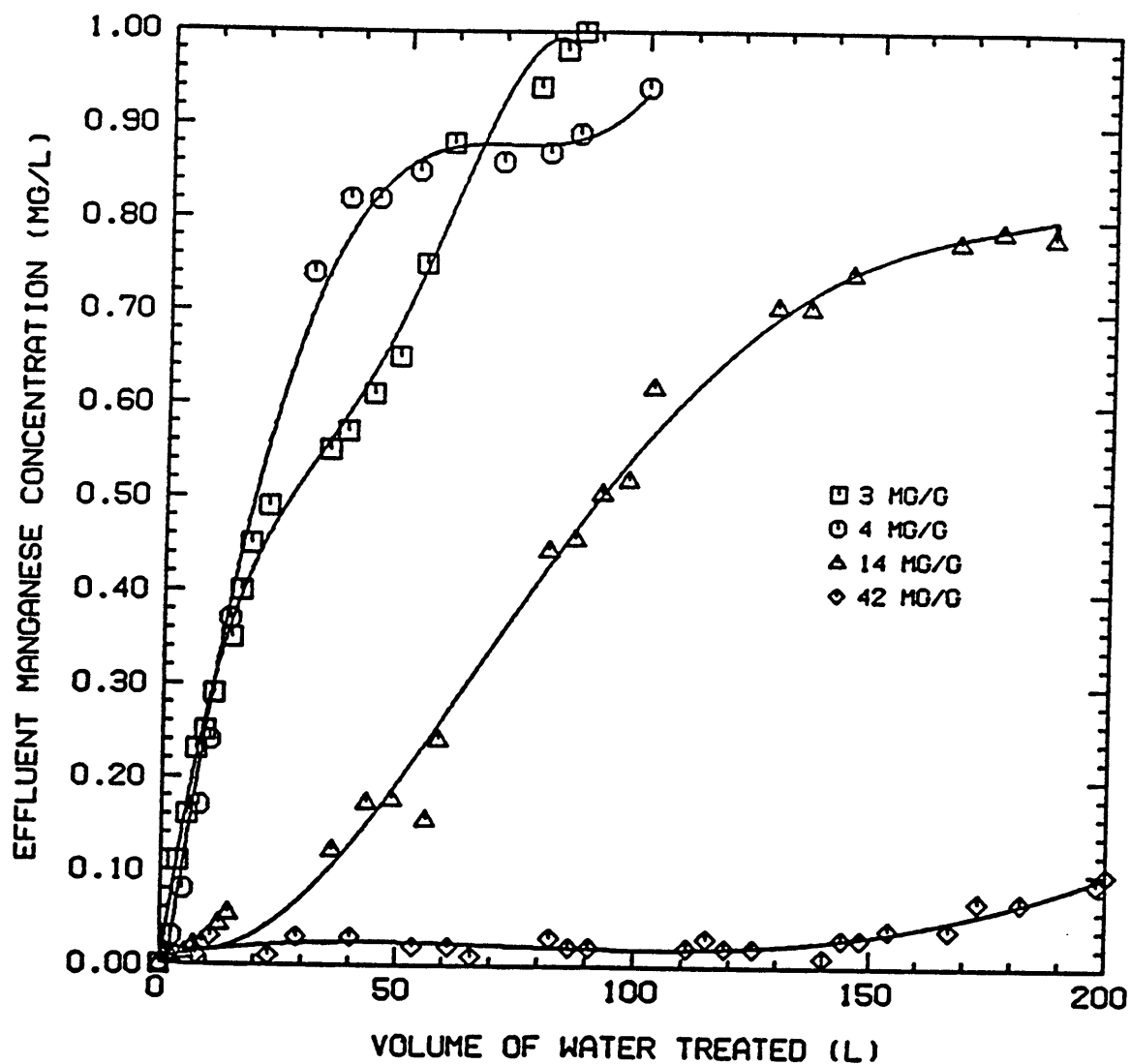


Figure 12. Effect of Surface Oxide Concentration on Mn (II) Uptake by Different Media at pH 7.8: [Influent Mn (II) = 1.0 mg/L; no HOCl in filter applied water; symbols denote surface extracted concentrations]

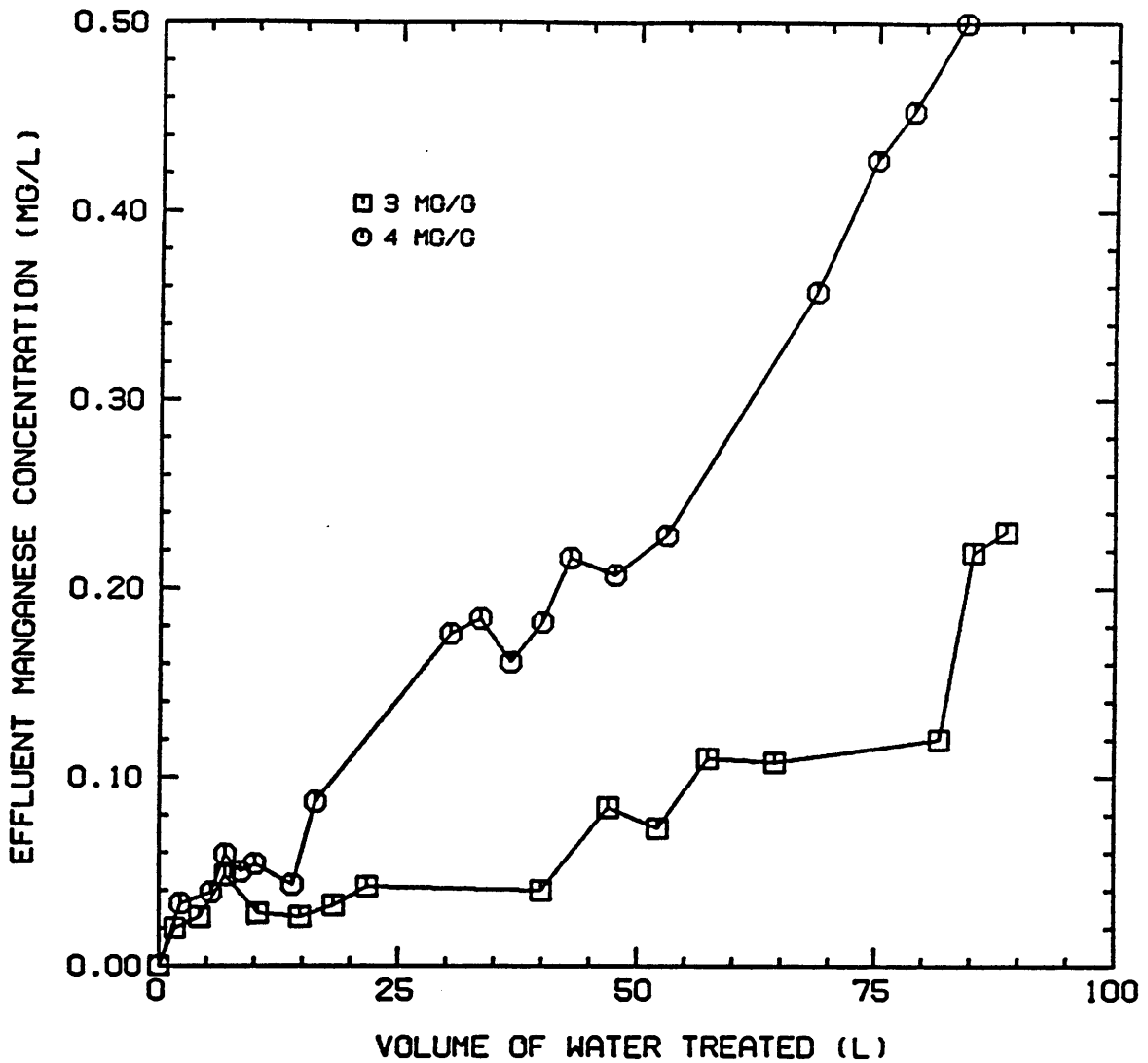


Figure 13. Effect of Surface Oxide Concentration on Mn (II) Uptake by Different Media at pH 8.8: [Influent Mn (II) = 1.0 mg/L; no HOCl in filter applied water; symbols denote surface extracted concentrations]

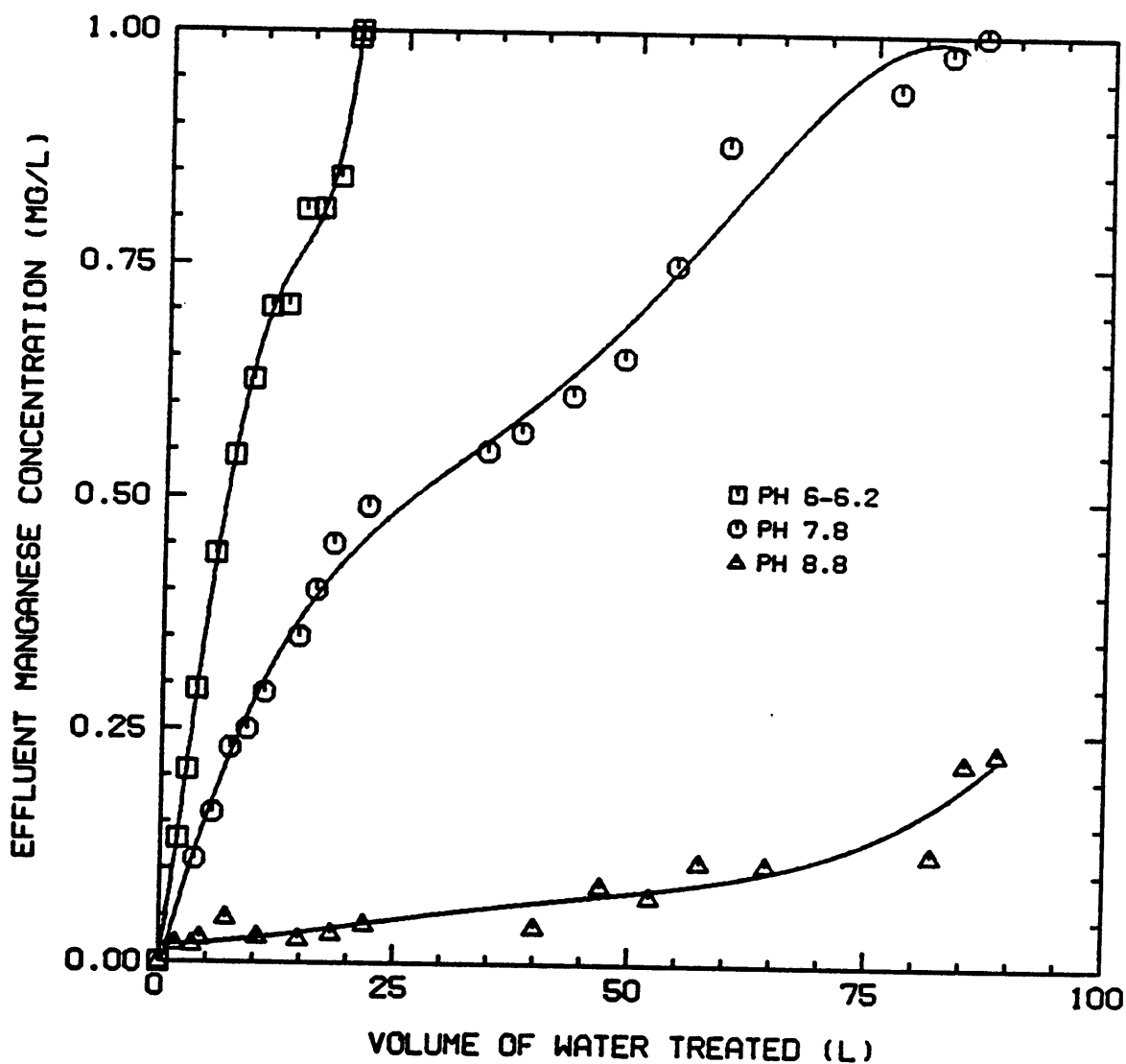


Figure 14. Effect of Solution pH upon Mn (II) Removal by Media #1 [3 mg/g Mn (II) on surface] in the Absence of Free Chlorine: [Influent Mn (II) = 1.0 mg/L]

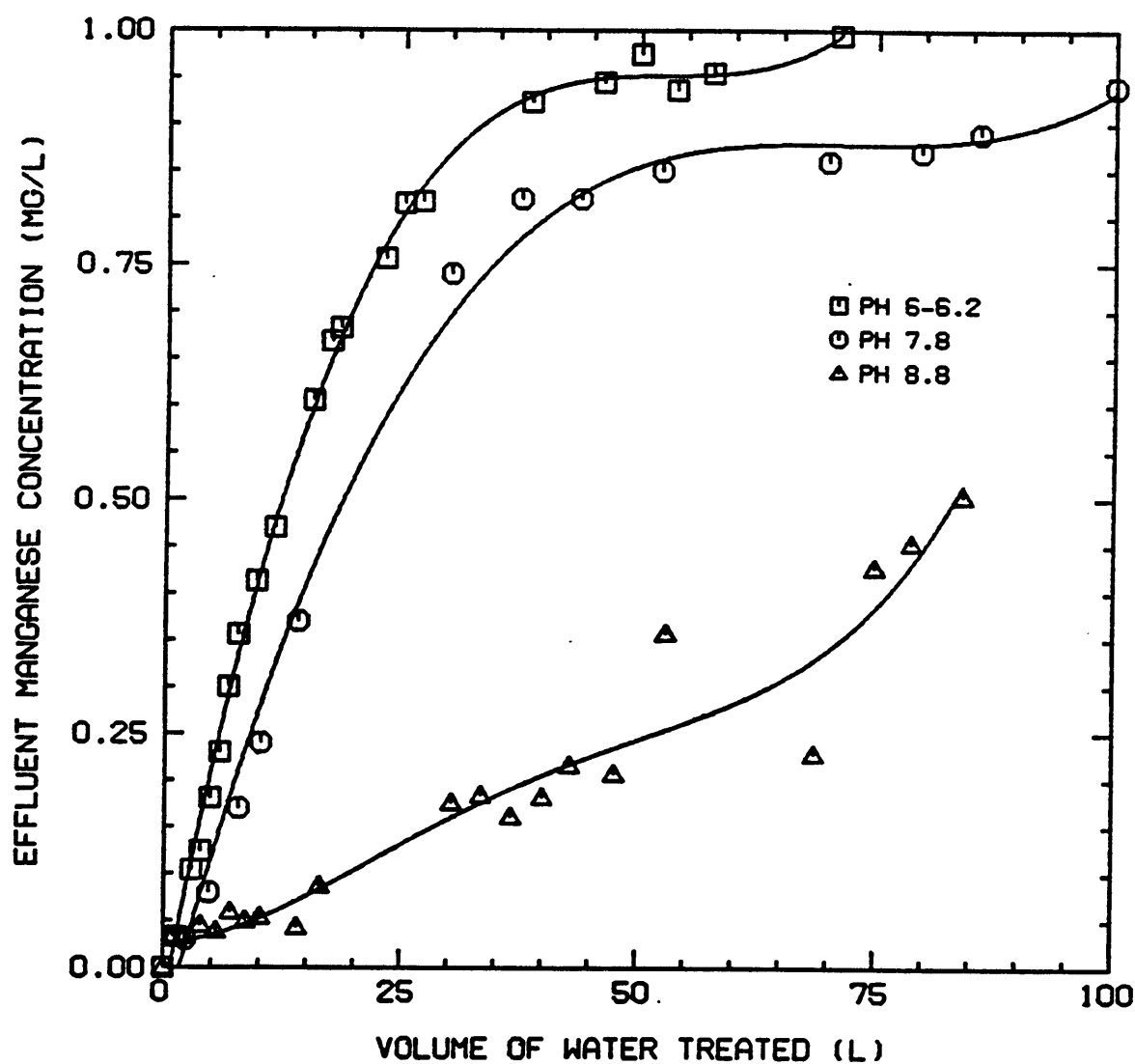


Figure 15. Effect of Solution pH upon Mn (II) Removal by Media #2 [4 mg/g Mn (II) on surface] in the Absence of Free Chlorine: [Influent Mn (II) = 1.0 mg/L]

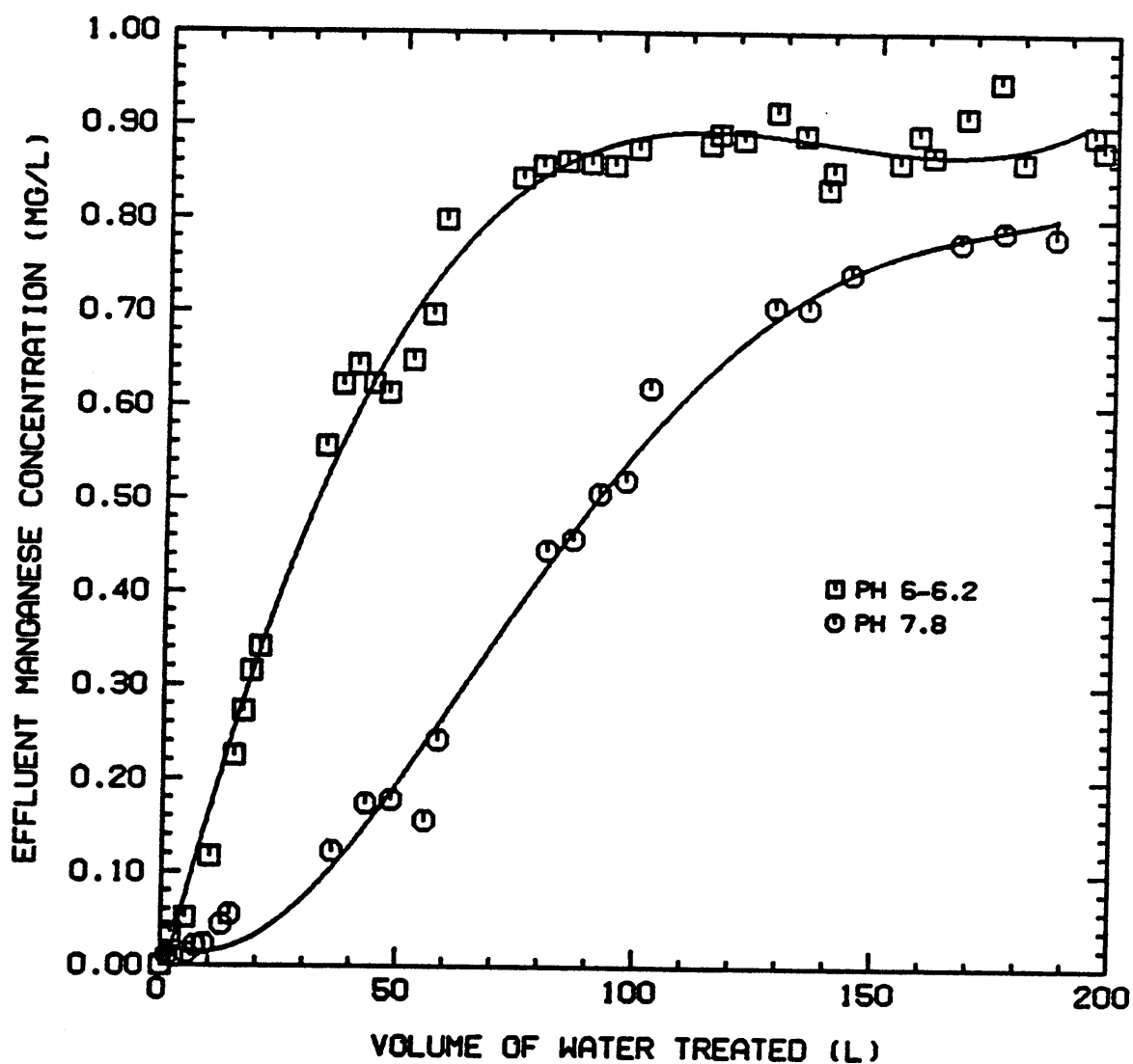


Figure 16. Effect of Solution pH upon Mn (II) Removal by Media #3 [14 mg/g Mn (II) on surface] in the Absence of Free Chlorine: [Influent Mn (II) = 1.0 mg/L]

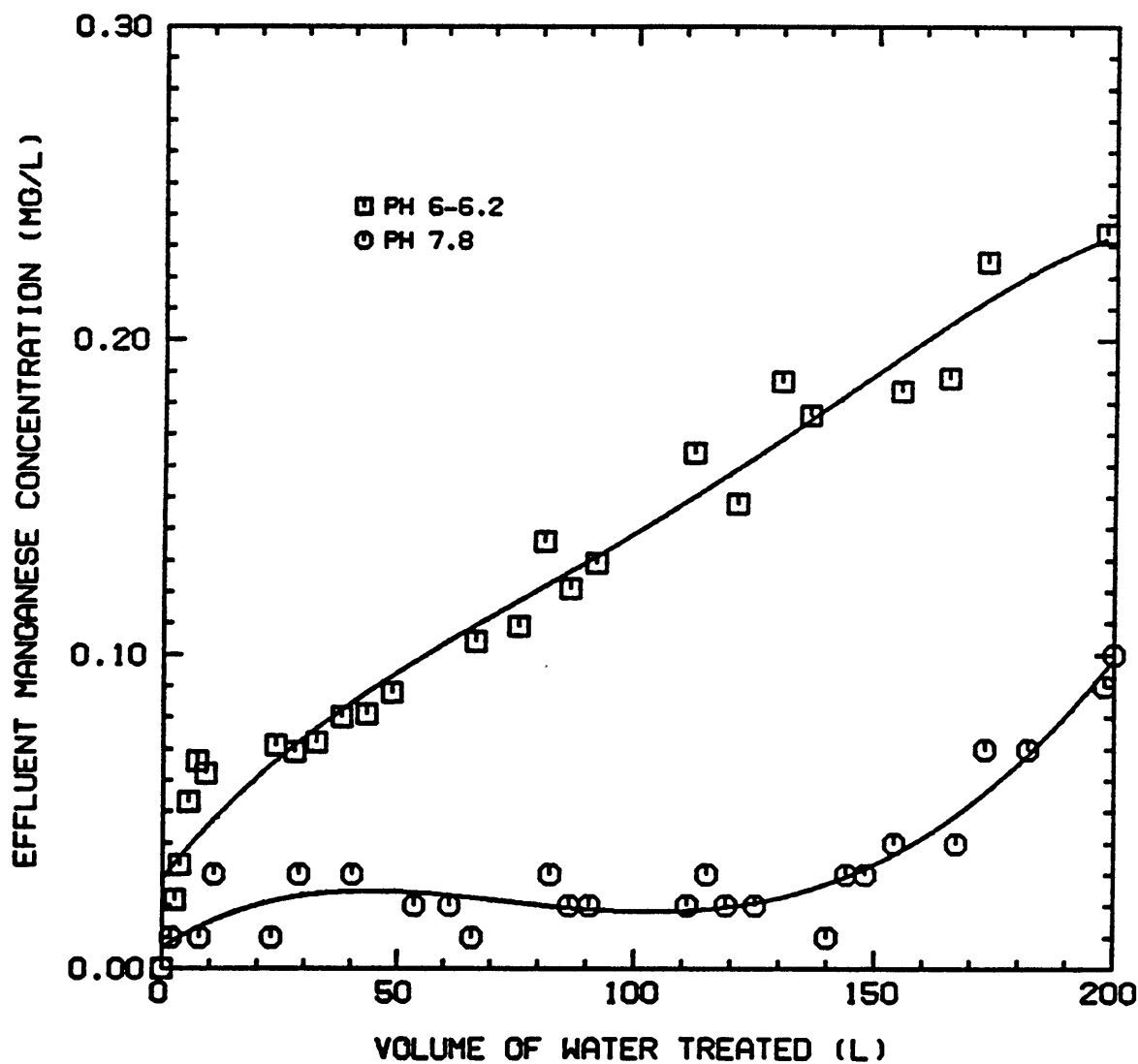


Figure 17. Effect of Solution pH upon Mn (II) Removal by Media #4 [42 mg/g Mn (II) on surface] in the Absence of Free Chlorine: [Influent Mn (II) = 1.0 mg/L]

Table 3. Amount of Mn (II) Removal for Different Media at Varying pH in the Absence of Free Chlorine (expressed in meq)

MEDIA SAMPLE #	INFLUENT pH	TOTAL Mn (II) UPTAKE (meq)
1 (3 mg/g)	6-6.2 7.8 8.8	0.30 1.09 2.80
2 (4 mg/g)	6 - 6.2 7.8 8.8	0.60 0.99 1.94
3 (14 mg/g)	6 - 6.2 7.8	1.53 3.00
4 (42 mg/g)	6 - 6.2 7.8	14.1 13.3*

*Note: Column study halted before complete exhaustion.

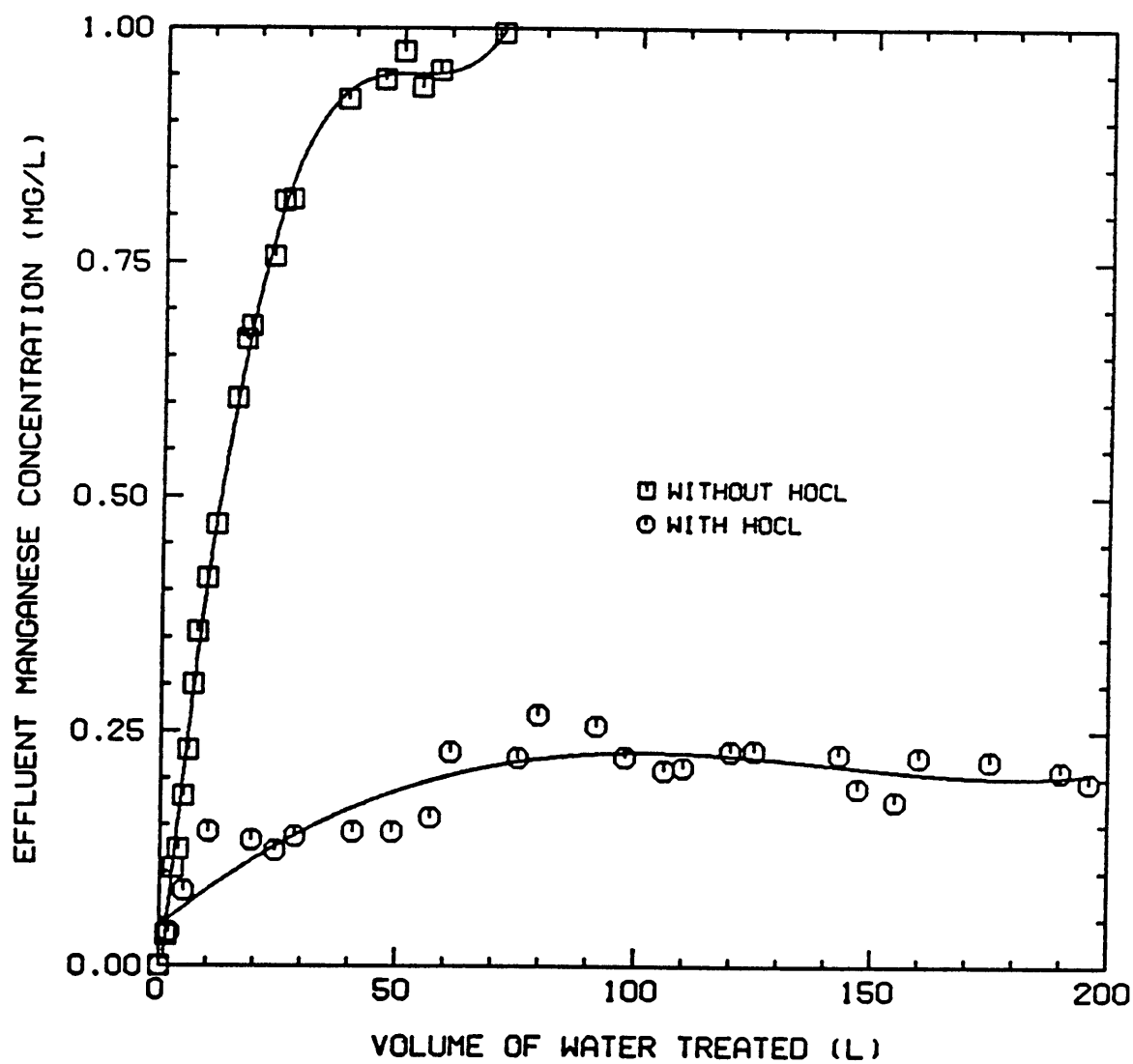


Figure 18. Mn (II) Uptake for Media #2 at pH 6-6.2 in the Absence and Presence of 2 mg/L HOCl in the Filter Applied Water: [Influent Mn (II) = 1.0 mg/L]

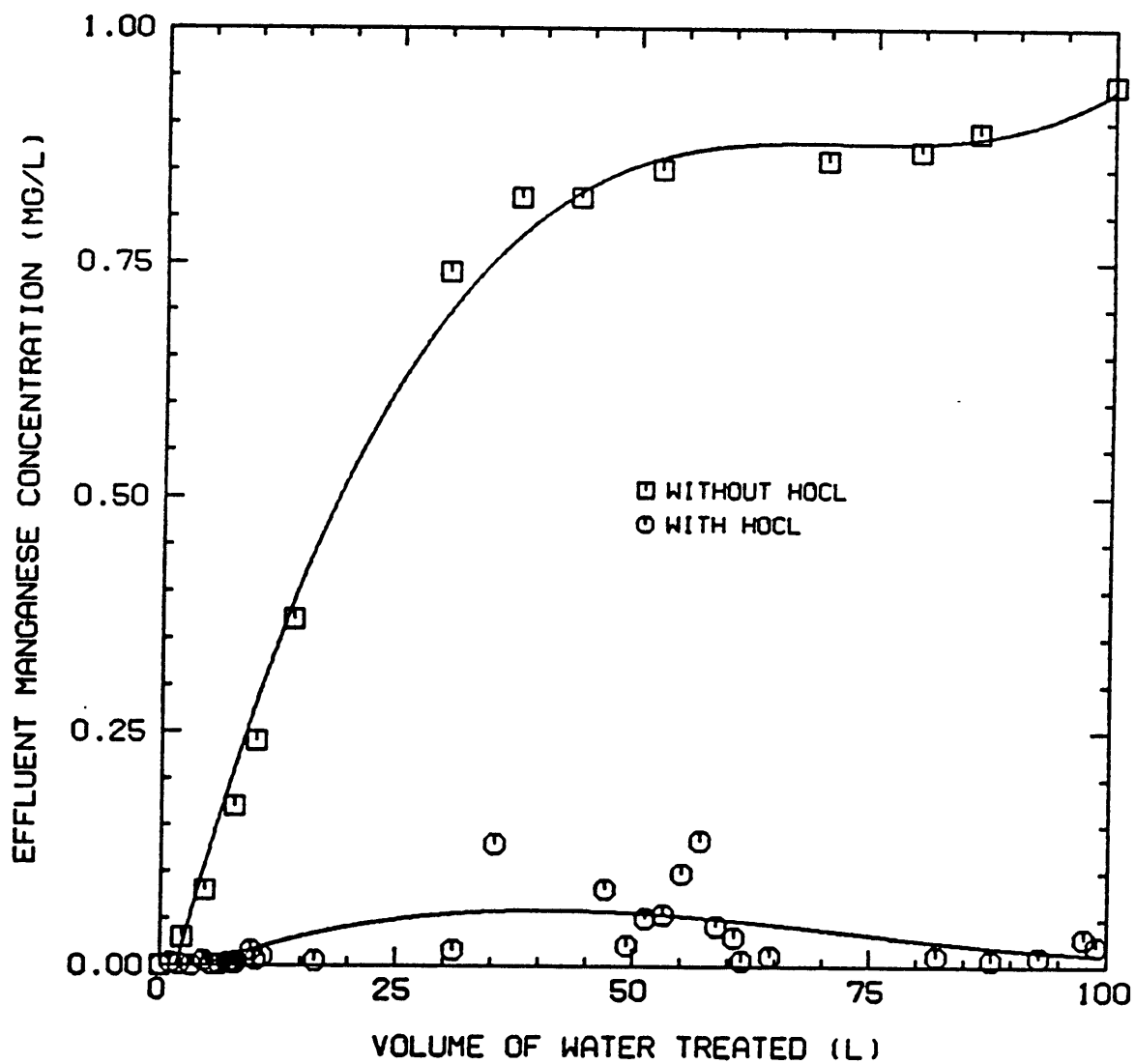


Figure 19. Mn (II) Uptake for Media #2 at pH 7.8 in the Absence and Presence of 2 mg/L HOCL in the Filter Applied Water: [Influent Mn (II) = 1.0 mg/L]

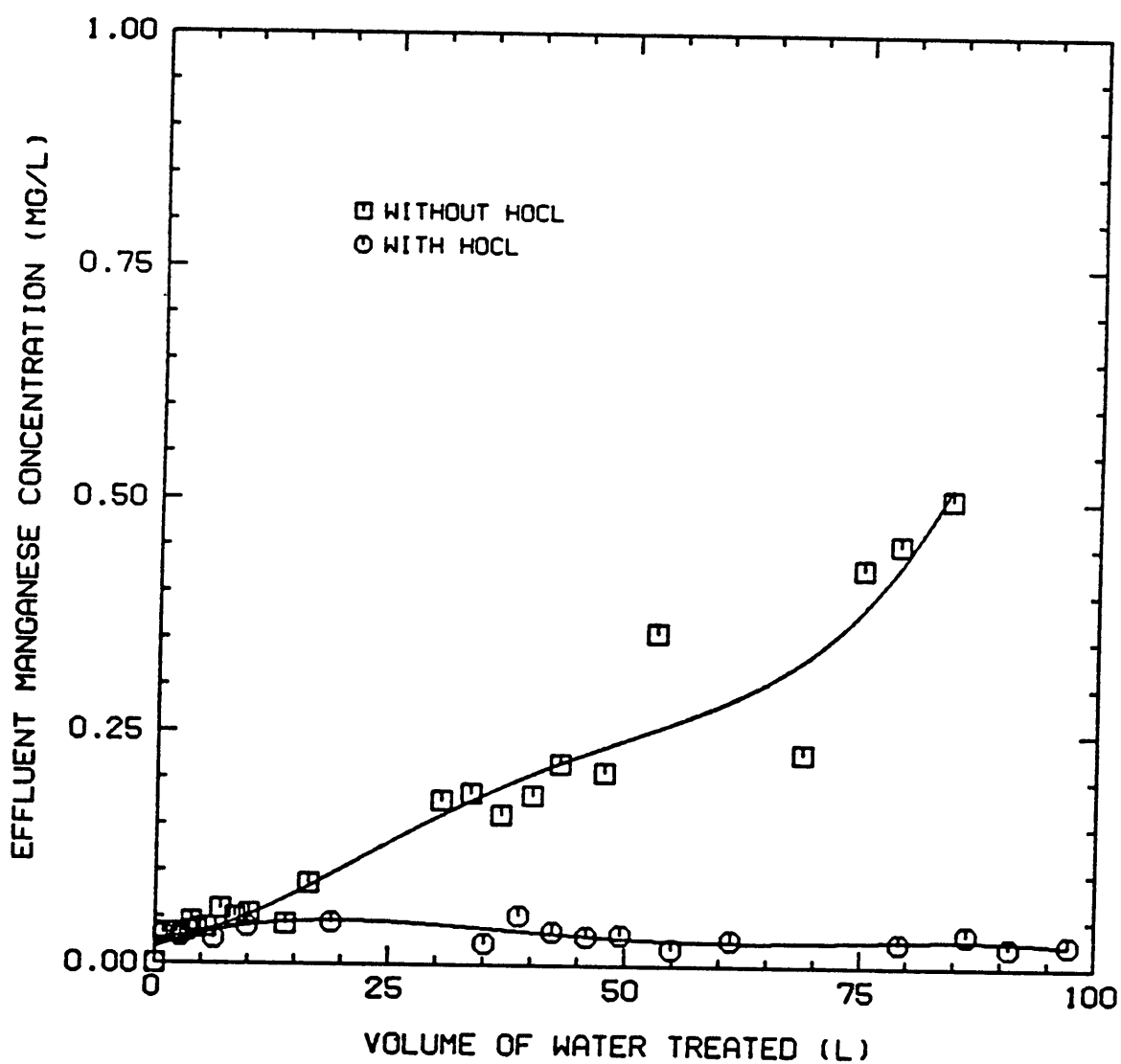


Figure 20. Mn (II) Uptake for Media #2 at pH 8.8 in the Absence and Presence of 2 mg/L HOCl in the Filter Applied Water: [Influent Mn (II) = 1.0 mg/L]

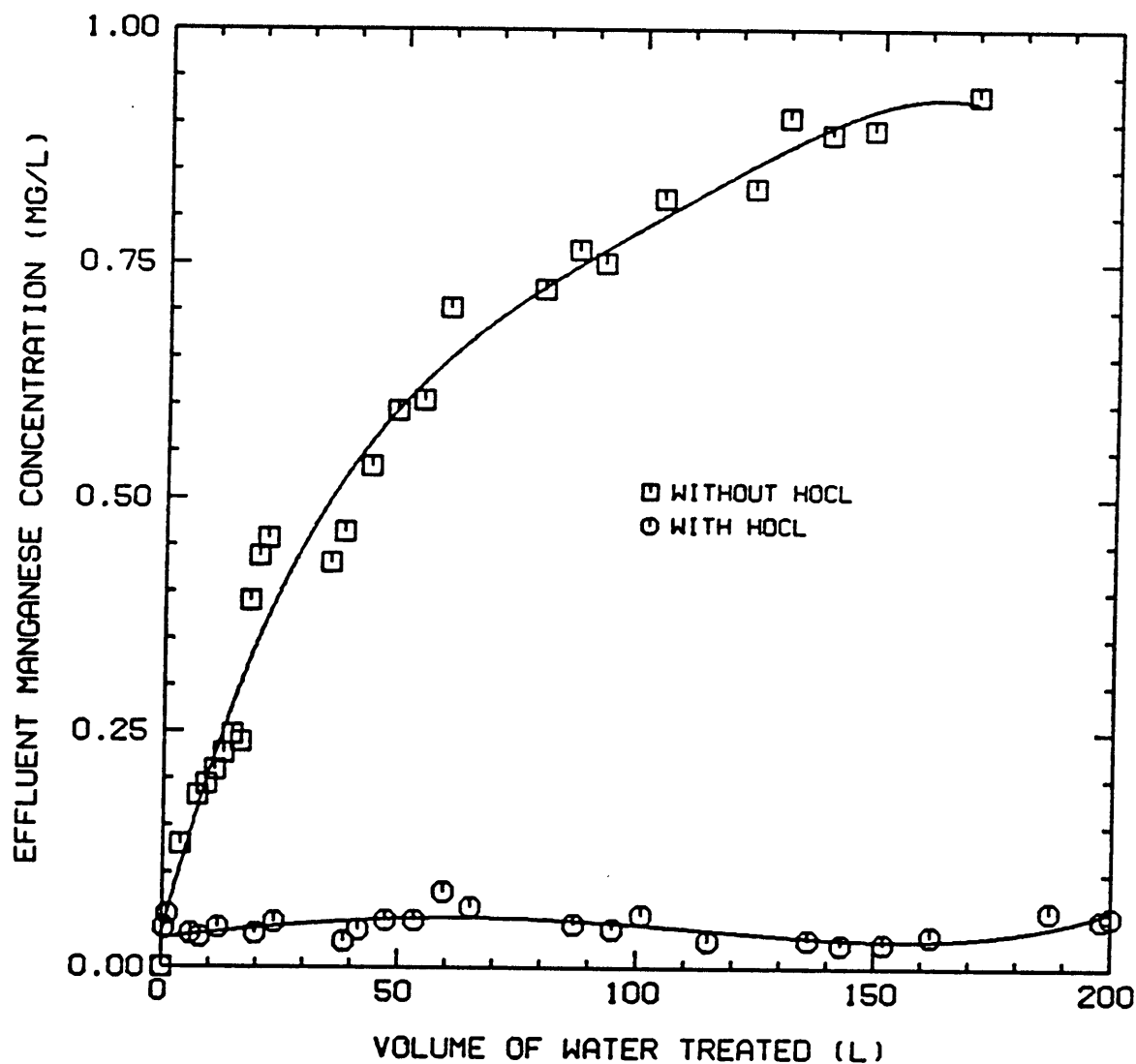


Figure 21. Mn (II) Uptake for Media #3 at pH 6-6.2 in the Absence and Presence of 2 mg/L HOCl in the Filter Applied Water: [Influent Mn (II) = 1.0 mg/L]

Table 4. Mn (II) Uptake in the Presence and Absence of 2 mg/L Free Chlorine
(expressed in meq; mg/g denote surface Mn conc.)

MEDIA SAMPLE #	INFLUENT pH	Mn (II) UPTAKE w/HOCl (meq)	Mn (II) UPTAKE w/o HOCl (meq)
1 (3 mg/g)	6-6.2 7.8 8.8	3.20 6.50 ---	0.30 1.09 2.80
2 (4 mg/g)	6-6.2 7.8 8.8	4.15 3.10 1.70*	0.60 0.99 1.94
3 (14 mg/g)	6-6.2 7.8	7.36 7.80	1.53 3.00
4 (42 mg/g)	6-6.2 7.8	10.7* ---	14.1 13.3

*Note: Column study halted before complete exhaustion.

Column Experiments in the Presence of Free Chlorine

Effects of Surface Oxide Concentration on Adsorption Capacity at Constant pH

The influence of free chlorine on manganese uptake by oxide-coated media is apparent in the data presented in this section. Note that a scale change in the y-axis was made to better illustrate the effluent manganese concentrations. The influent manganese concentration remained at 1.0 mg/L for all studies; free chlorine concentrations were applied at 2.0 mg/L. Figures 22 and 23 represent manganese removal data for different media at pH 6-6.2 and 7.8, respectively. Research into the effects of higher pH conditions on Mn^{2+} removal was not conducted due to problems of Mn^{2+} oxidation by HOCl prior to the filter which plugged the columns. This issue will be expanded on further in the discussion section.

Effects of pH on Adsorption Capacity for Oxide-Coated Filter Media

Three of the four media were examined for their uptake ability in the presence of free chlorine at different pH values. Figure 24 presents results from media #1 (3 mg/g surface oxide concentration) with free chlorine at pH 6-6.2 and 7.8. Again the y-axis has been expanded to 0.3 mg/L effluent manganese concentration to better show the results from these particular studies. Data on media #2 (4 mg/g surface oxide concentration) with 2 mg/L HOCl in the filter applied water are represented in Figure 25 at pH 6-6.2, 7.8 and 8.8. However, Figure 26 depicts media #3 which has a much larger amount of oxide coating (14 mg/g) under the effects of a continuous HOCl feed solution at pH 6-6.2 and 7.8. A summary of the data from studies with and without chlorine for different media at varying pH conditions has been presented in Table 4.

Manganese and Chlorine Relationships

The relationship of Mn (II) uptake with the amount of free chlorine consumed is represented in Figures 27-31. In these plots the right y-axis presents the effluent chlorine

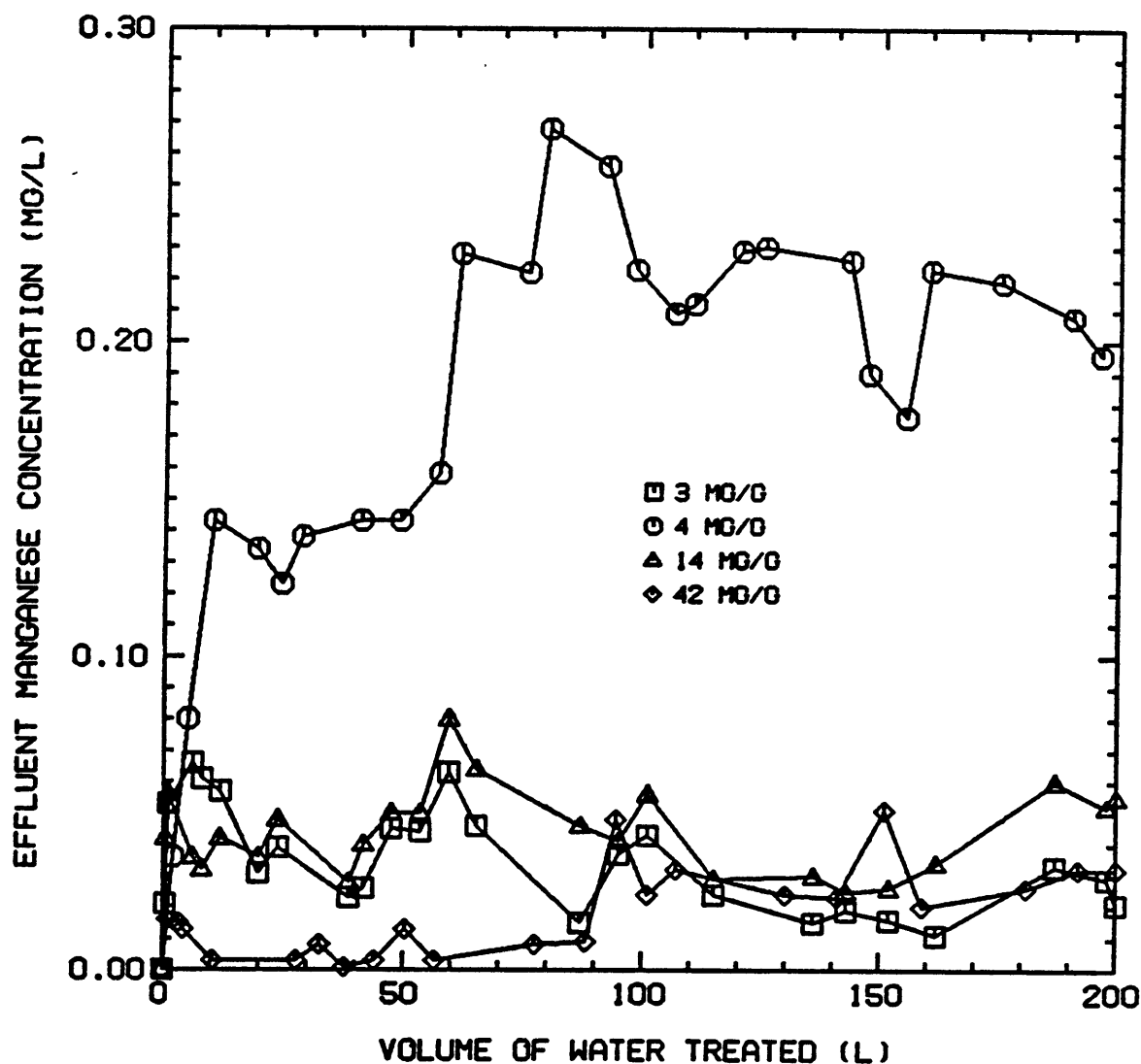


Figure 22. Effect of Surface Oxide Concentration on Mn (II) Uptake by Different Media at pH 6-6.2 in the Presence of 2 mg/L HOCl: [Influent Mn (II) = 1.0 mg/L; symbols denote surface extracted concentration]

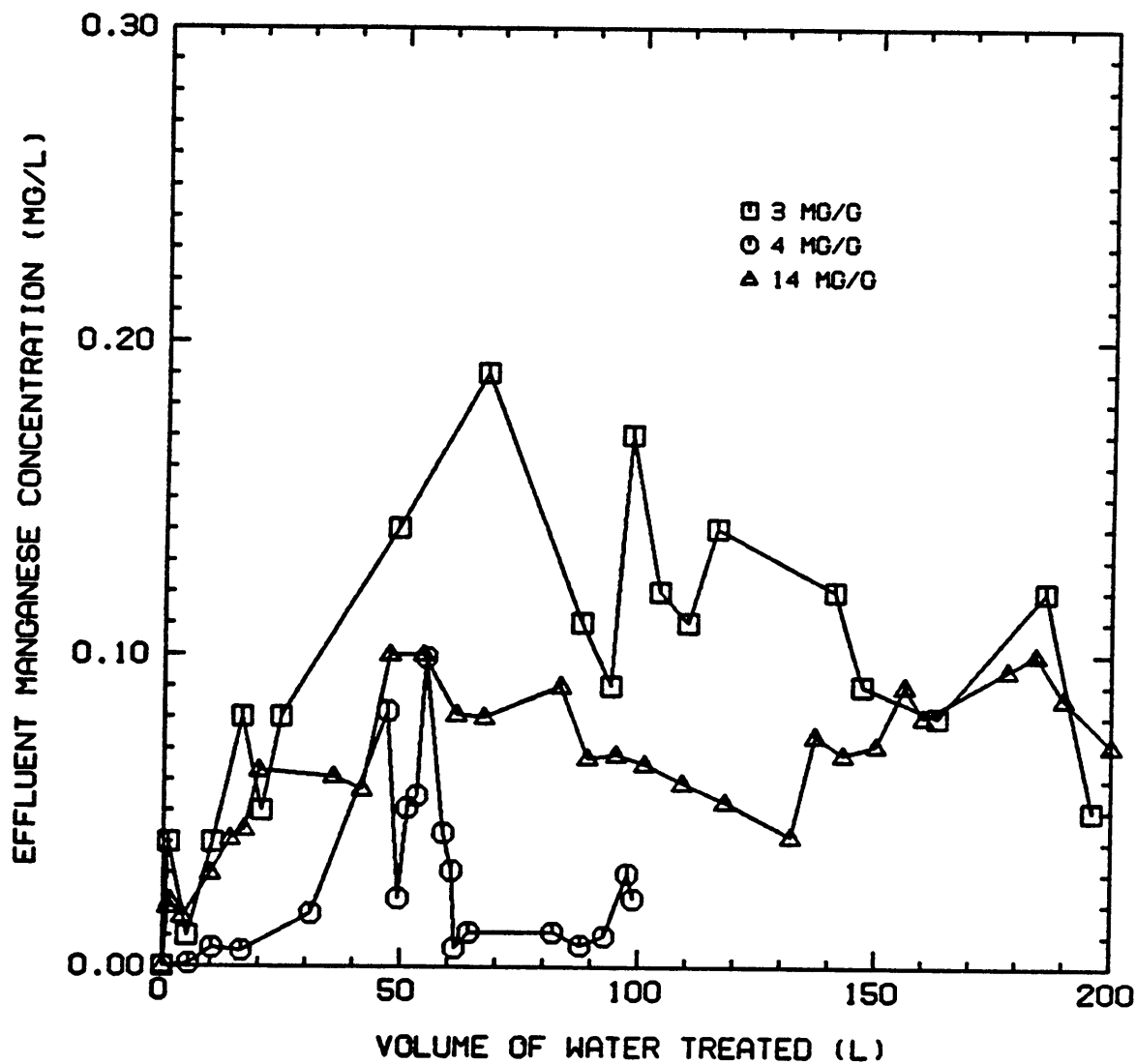


Figure 23. Effect of Surface Oxide Concentration on Mn (II) Uptake by Different Media at pH 7.8 in the Presence of 2 mg/L HOCl: [Influent Mn (II) = 1.0 mg/L; symbols denote surface extracted concentration]

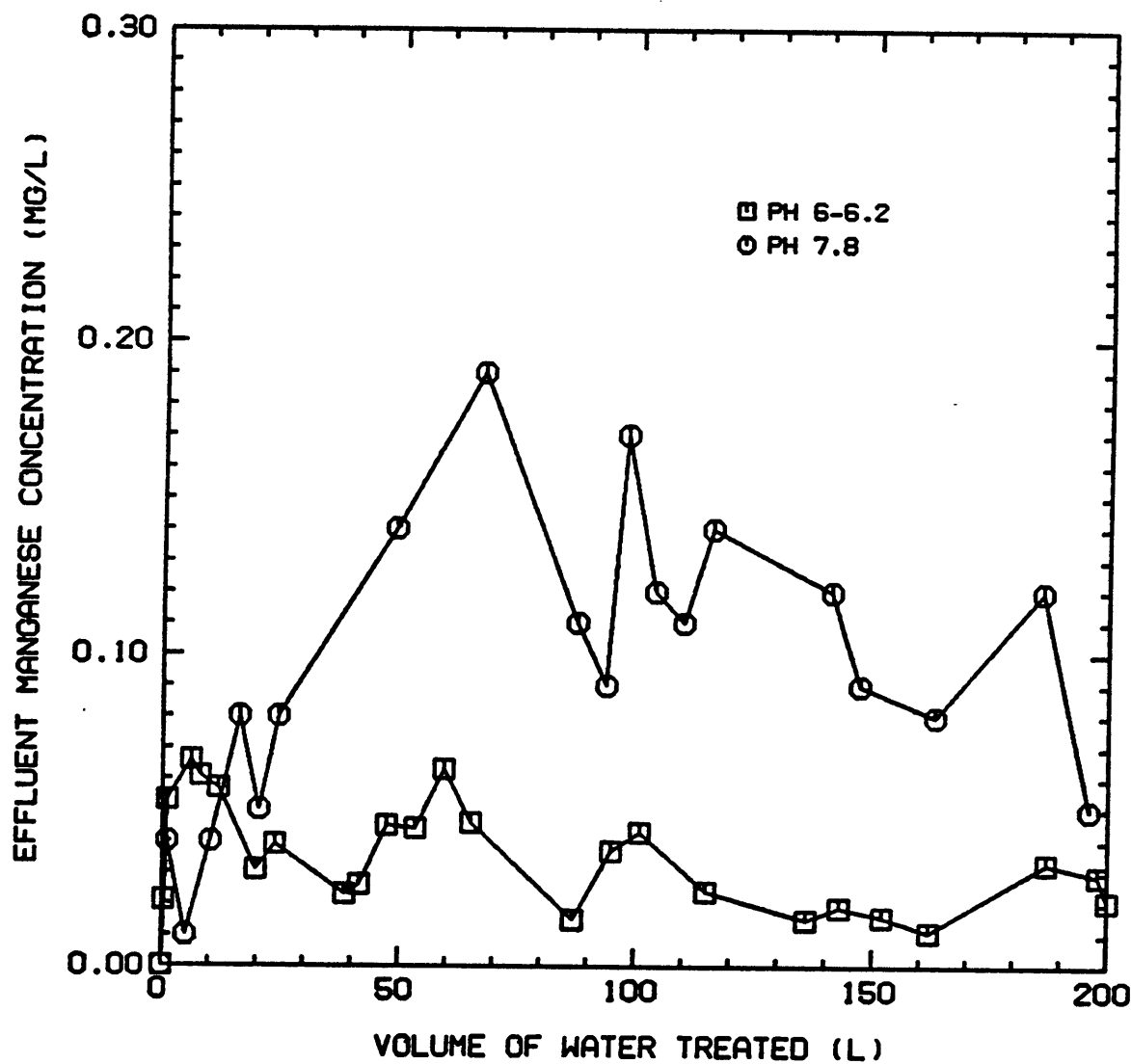


Figure 24. Effect of Solution pH upon Mn (II) Removal by Media #1: [3 mg Mn (II)/g of media on the surface; 2 mg/L HOCl in the filter applied water; Influent Mn (II) = 1.0 mg/L]

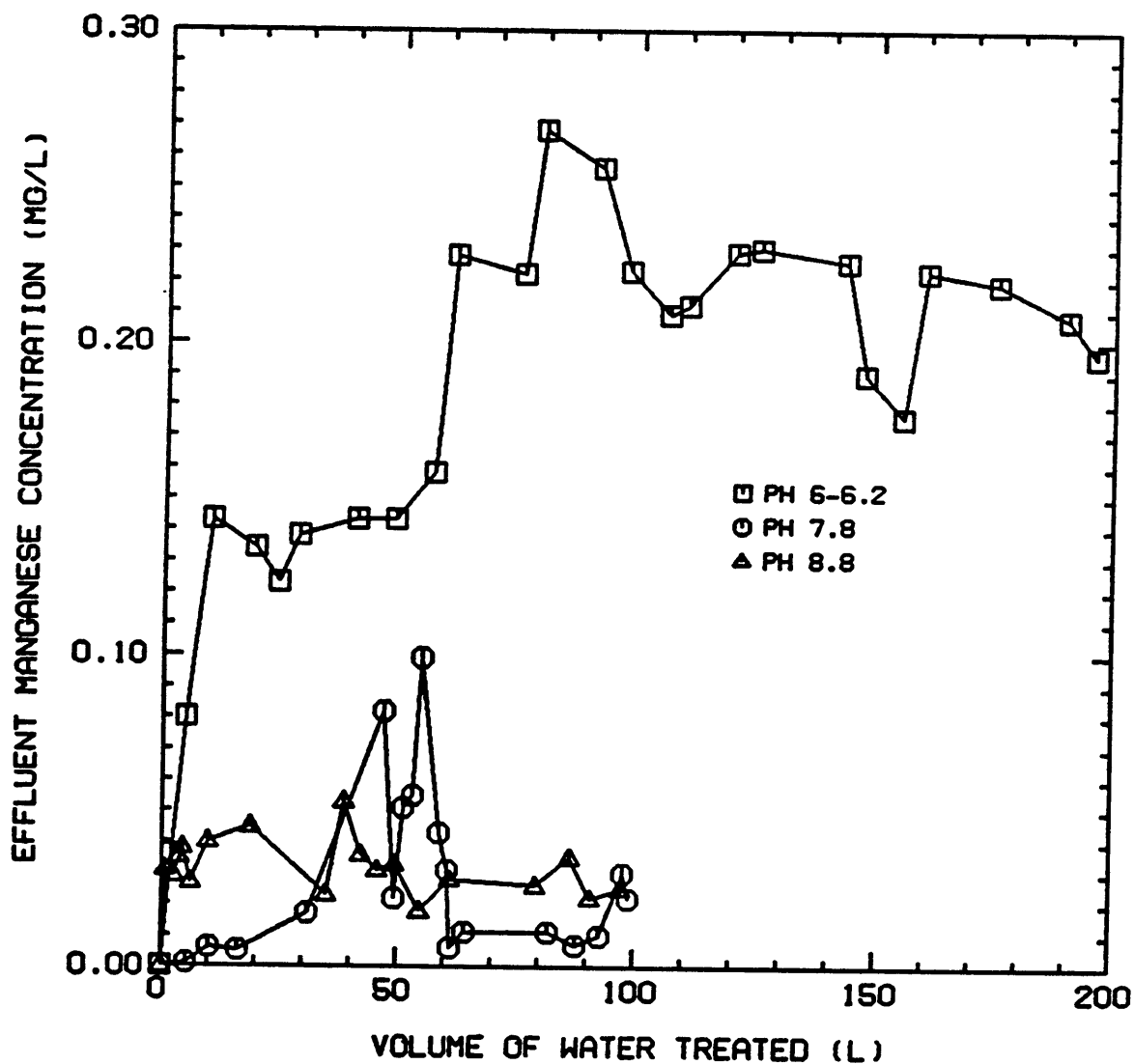


Figure 25. Effect of Solution pH upon Mn (II) Removal by Media #2: [4 mg Mn (II)/g of media on the surface; 2 mg/L HOCl in the filter applied water; Influent Mn (II) = 1.0 mg/L]

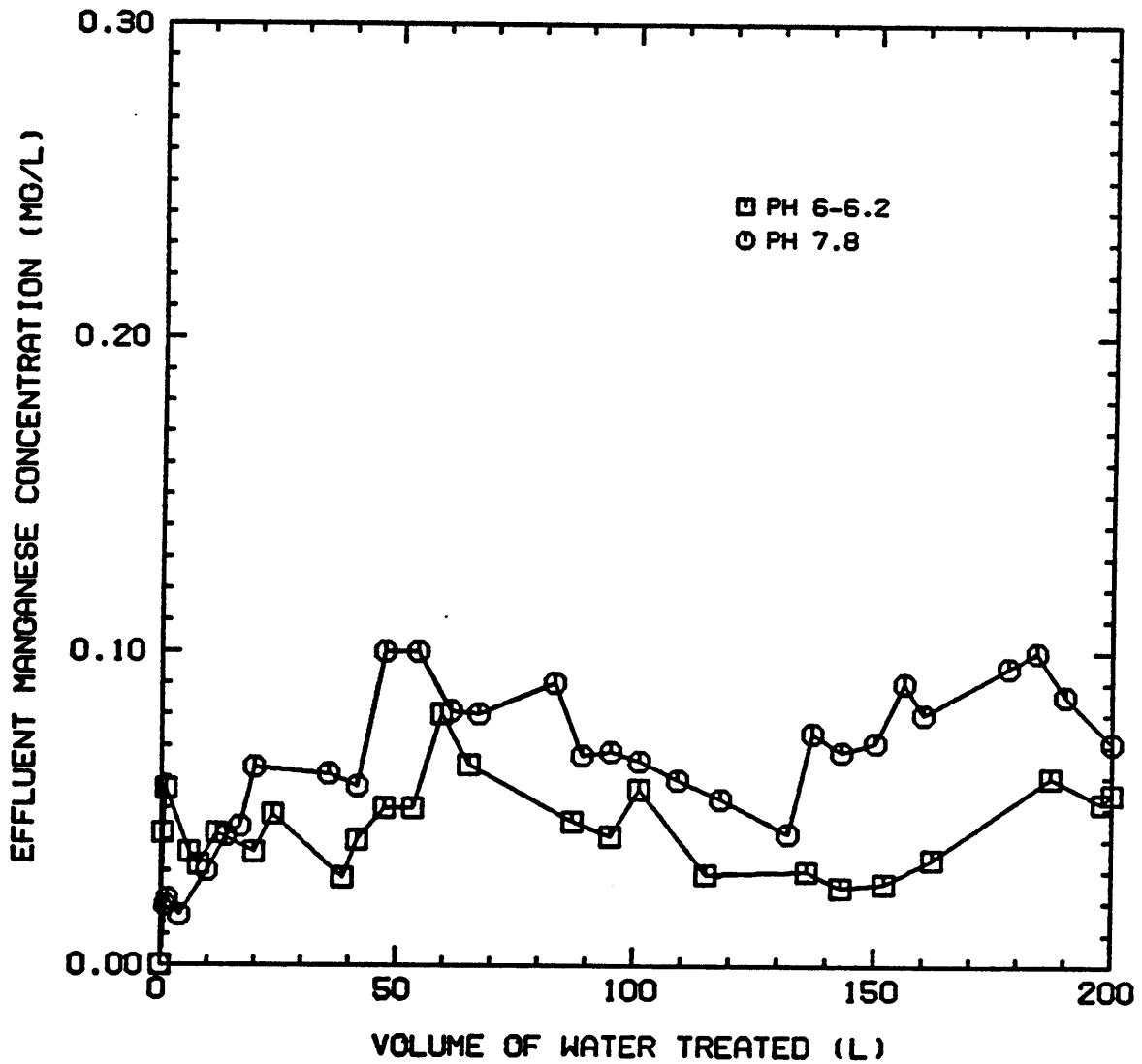


Figure 26. Effect of Solution pH upon Mn (II) Removal by Media #3: [14 mg Mn (II)/g of media on the surface; 2 mg/L HOCl in the filter applied water; Influent Mn (II) = 1.0 mg/L]

concentrations or residual chlorine. Influent chlorine concentrations were maintained 2 mg/L. Data included in Figures 27 and 28 show effluent Mn (II) and residual chlorine relationships for media #1 at pH 6-6.2 and 7.8, respectively. The results of Mn (II) uptake with the amount of chlorine consumed for media #3 at pH 6-6.2 and 7.8 are depicted in Figures 29 and 30. Again the difference in media #1 from media #3 is the amount of oxide coating present on the surface of the media. Results for the largest, oxide-coated media (media #4; 42 mg/g) are reported in Figure 31. The results from these experiments are summarized in Table 5 and compare the Mn (II) uptake in the presence of free chlorine with the amount of free chlorine consumed during the Mn (II) removal process.

The research emphasis was aimed at Mn (II) removal studies in the presence and absence of free chlorine. The effect of this oxidant was quite apparent in the reported data. The two basic parameters investigated were the effects of media oxide coating concentration and influent pH. Relationships between the amount of manganese removed with the amount of free chlorine consumed were also presented. To further investigate the mechanisms for Mn (II) uptake, KMnO_4 demands on oxide-coated filter media and acid backtitrations of the exhausted filter columns were also performed. Data from these experiments are reported in the next two subsections.

Potassium Permanganate Demands of Oxide-Coated Filter Media

The KMnO_4 demands of the surface oxide coating of the filter media were performed for both columns with and without chlorine. With a continuous supply of chlorine fed to the column, the KMnO_4 demand of the oxide-coating for these columns should theoretically be less than the columns operated without chlorine as the demand for an oxidant should have been met by the continuous supply of chlorine. The data reported in this section are summarized in Table 6. The KMnO_4 demands of the oxide-coated filter

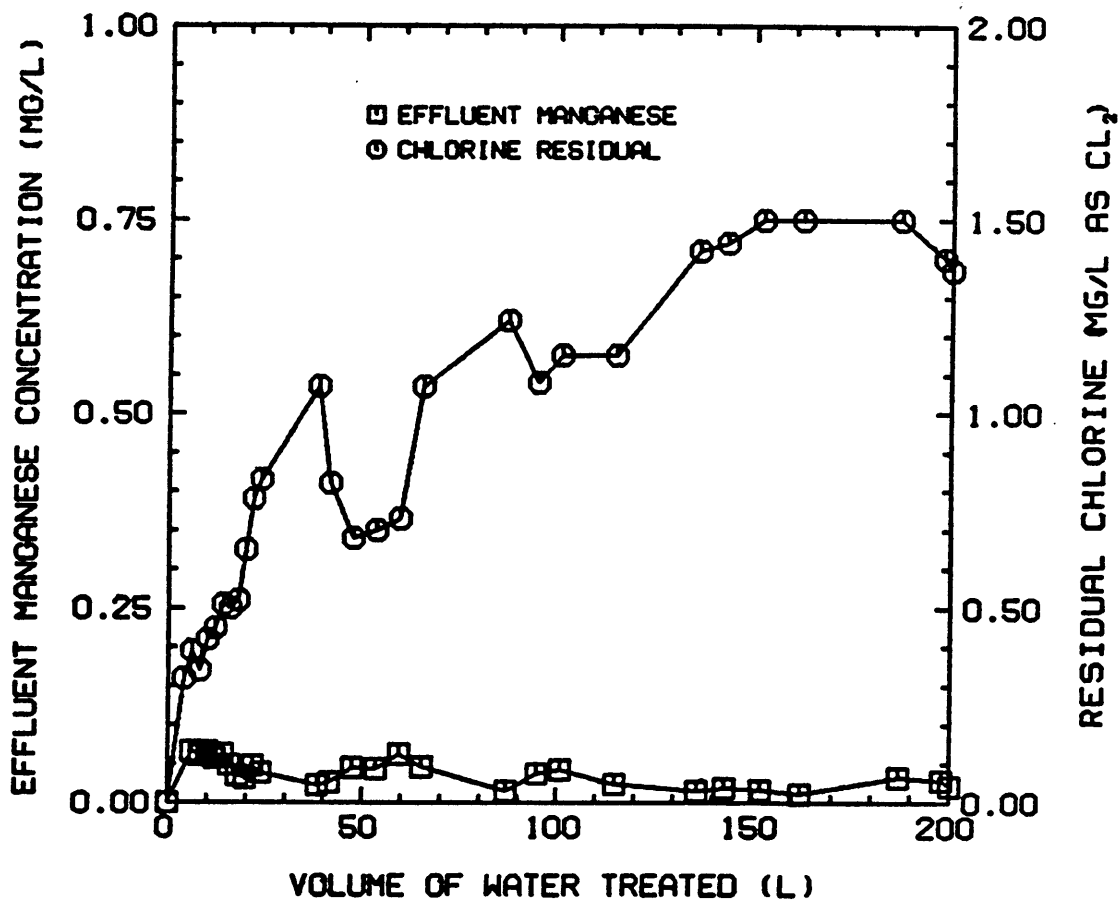


Figure 27. Effluent Manganese and Residual Chlorine Relationships for Media #1 at pH 6-6.2: [Influent Mn (II) = 1.0 mg/L; Influent HOCl = 2 mg/L]

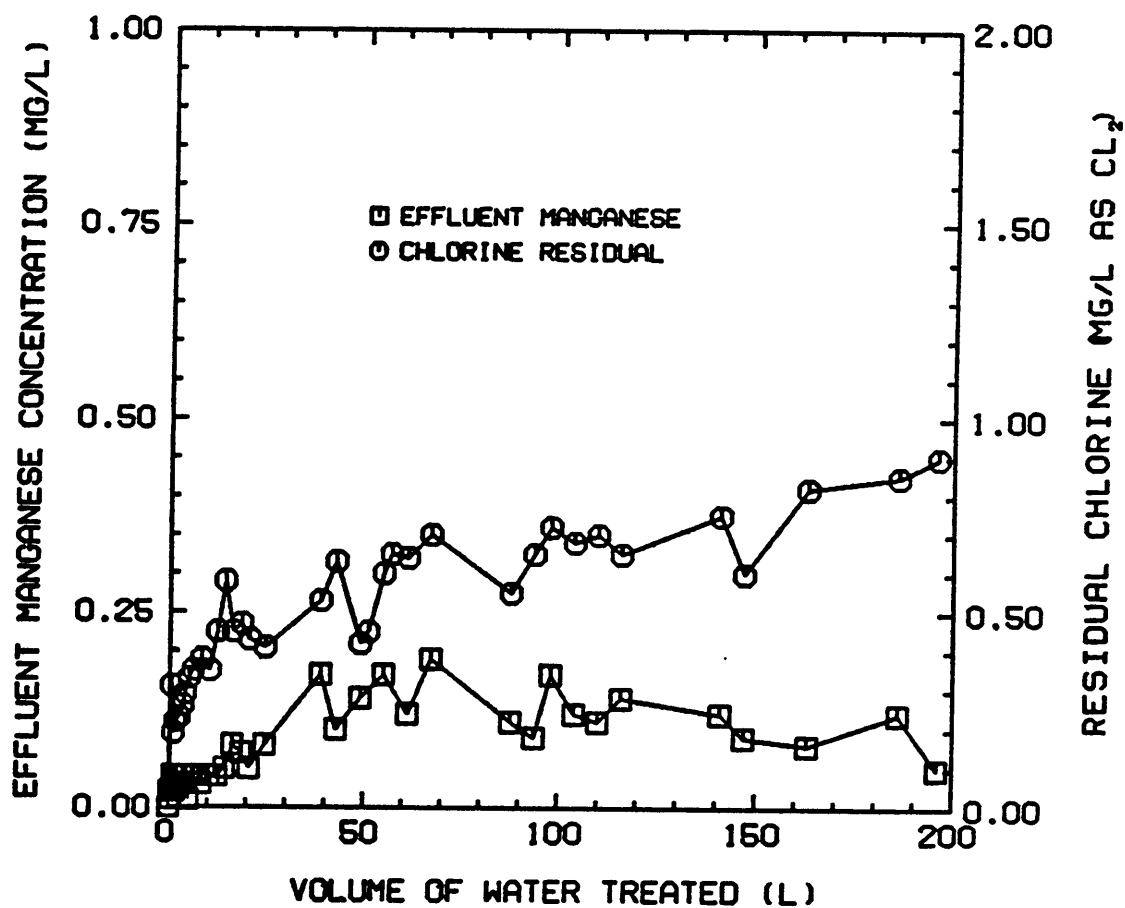


Figure 28. Effluent Manganese and Residual Chlorine Relationships for Media #1 at pH 7.8: [Influent Mn (II) = 1.0 mg/L; Influent HOCl = 2 mg/L]

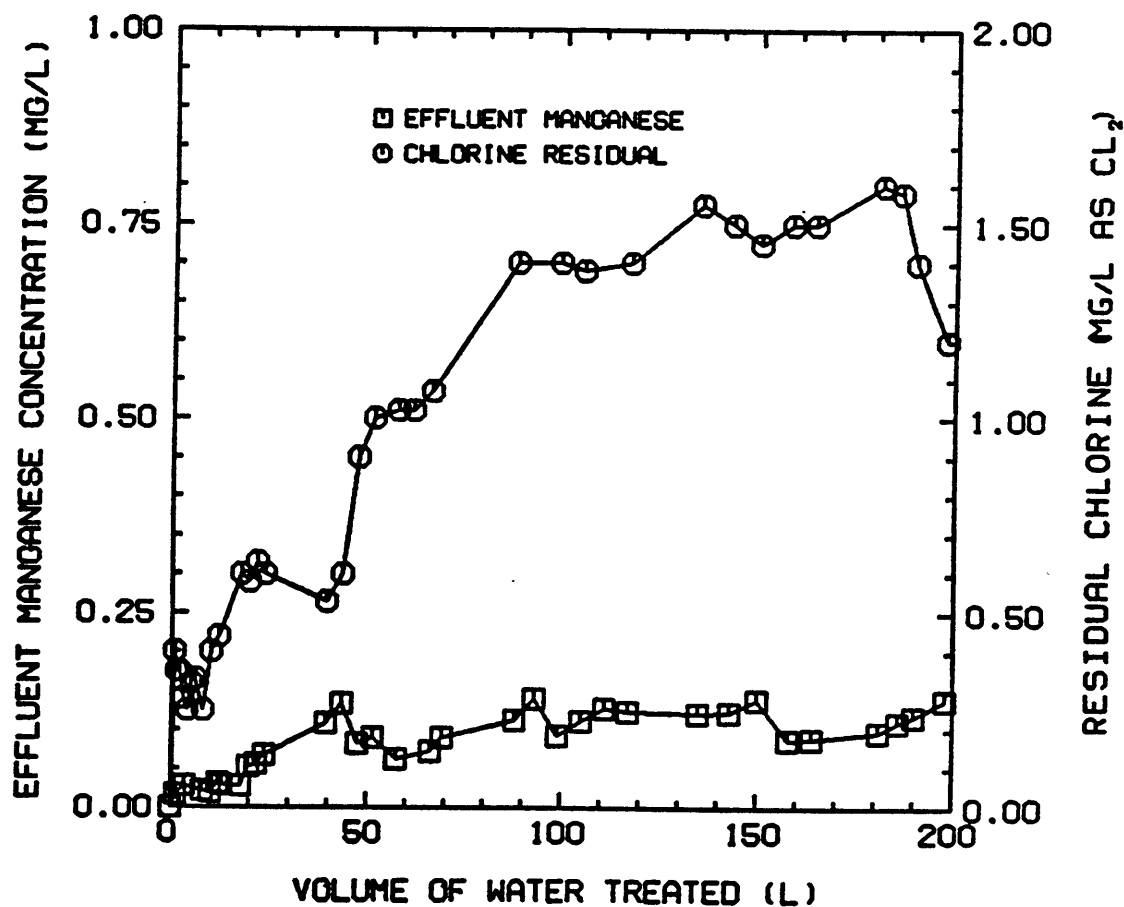


Figure 29. Effluent Manganese and Residual Chlorine Relationships for Media #3 at pH 6-6.2: [Influent Mn (II) = 1.0 mg/L; Influent HOCl = 2 mg/L]

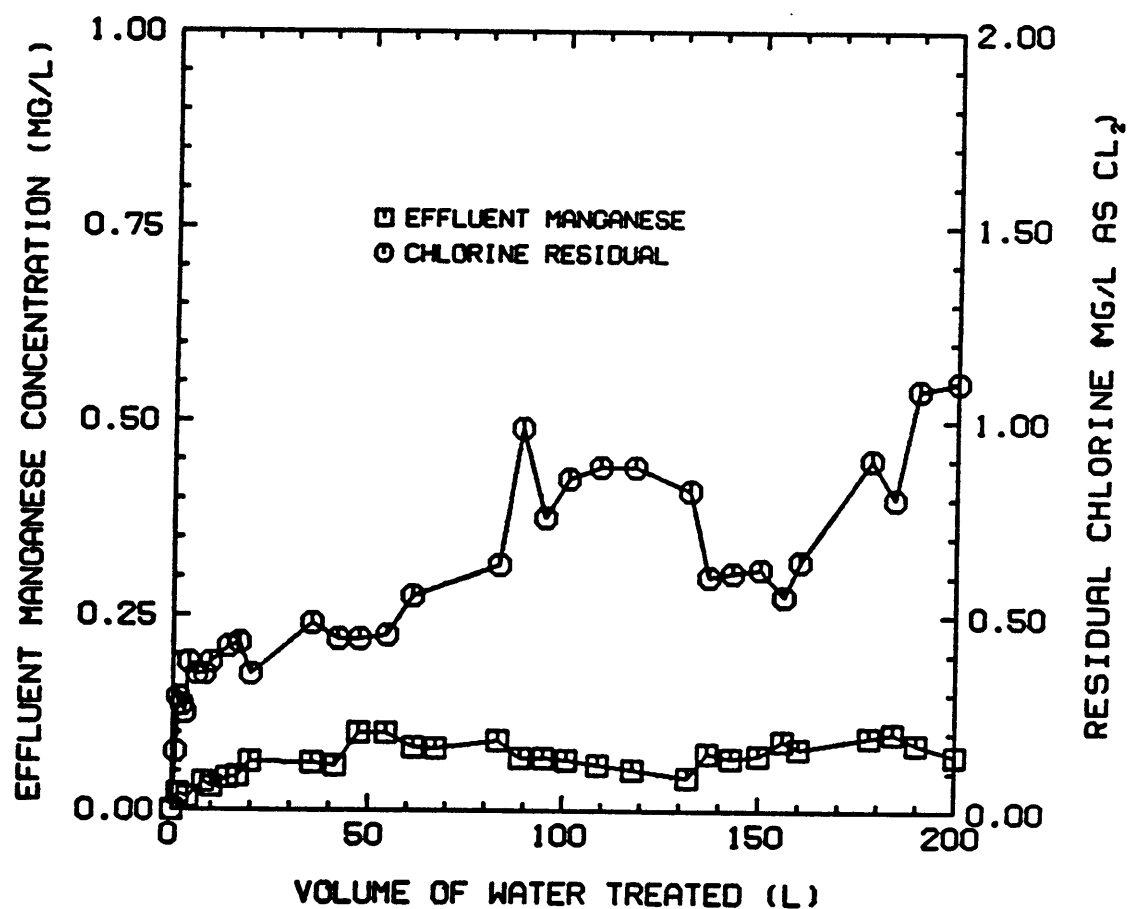


Figure 30. Effluent Manganese and Residual Chlorine Relationships for Media #3 at pH 7.8: [Influent Mn (II) = 1.0 mg/L; Influent HOCl = 2 mg/L]

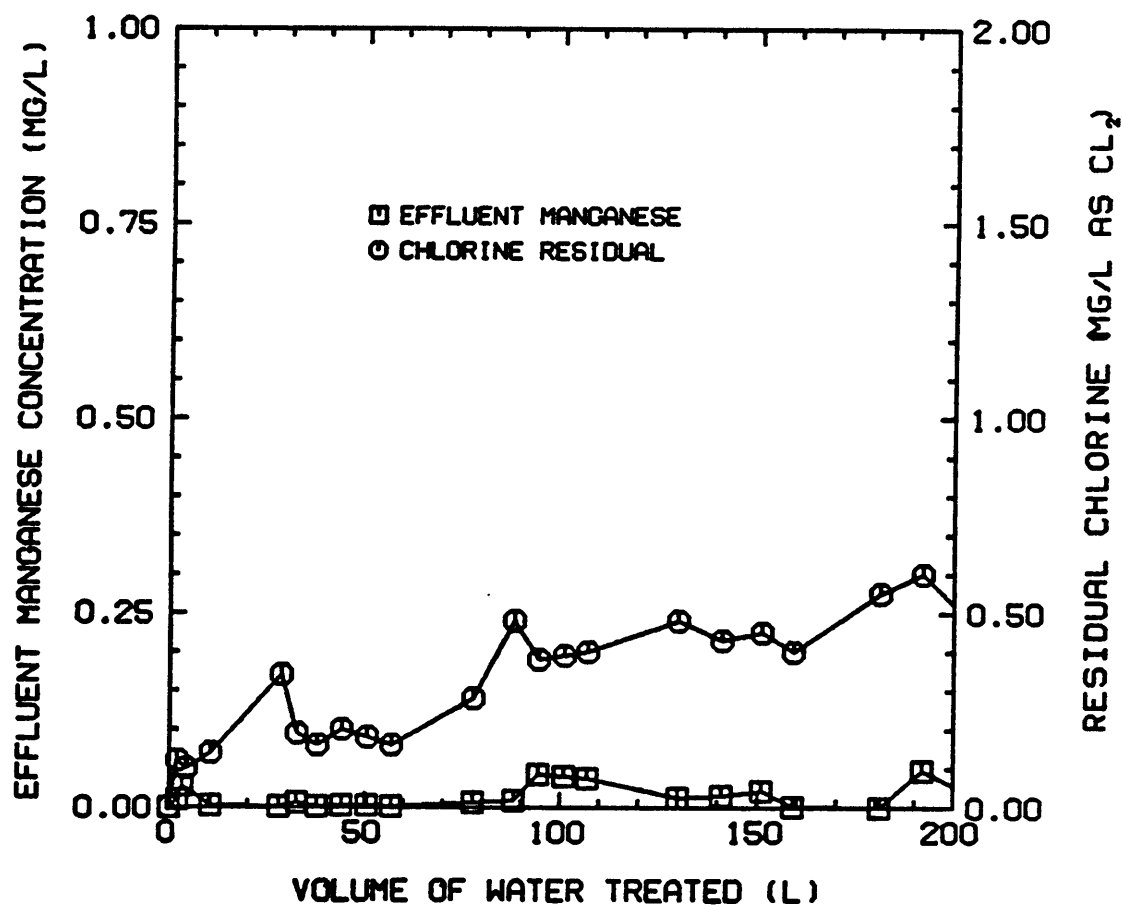


Figure 31. Effluent Manganese and Residual Chlorine Relationships for Media #4 at pH 6-6.2: [Influent Mn (II) = 1.0 mg/L; Influent HOCl = 2 mg/L]

Table 5. Relationship of Mn (II) Uptake to Free Chlorine Consumed for Different Media at Varying pH

MEDIA SAMPLE #	INFLUENT pH	Mn (II) UPTAKE w/HOCl (meq)	HOCl DEMAND (meq)
1 (3 mg/g)	6-6.2 7.8 8.8	4.15 3.10 1.70	4.40 2.80 1.78
2 (4 mg/g)	6-6.2 7.8	3.20 6.50	1.73 7.50
3 (14 mg/g)	6-6.2 7.8	7.36 7.80	5.75 9.10
4 (42 mg/g)	6-6.2	10.7*	10.3

*Note: Column study halted before complete exhaustion

media for columns with and without chlorine are given for different media at varying pH. Note that the amount of chlorine taken up or the chlorine demand is also given for columns operated with chlorine.

A final experiment in this area of study was conducted to help explain the KMnO_4 demand seen in columns operated in the presence of chlorine. An extended chlorine feed with no influent Mn (II) and subsequent KMnO_4 demand was performed to ascertain if the manganese adsorbed just prior to stopping the column was accounting for the observed KMnO_4 demand in columns with HOCl present in the feed water. Table 7 represents the data from this experiment. The results indicate that an extended chlorine feed would help to oxidize the remaining adsorbed Mn^{2+} and the demand of the oxide-coated filter media for KMnO_4 would decrease.

Release of Mn^{2+} from Oxide-Coated Filter Media

Data further investigating the mechanisms for manganese uptake in the presence and absence of chlorine are presented in this section. Once KMnO_4 demand testing had been completed, studies investigating the potential release of surface adsorbed Mn (II) were conducted. A pH 5.0 solution of dechlorinated Blacksburg tap water was fed through the column following completion of Mn (II) uptake experiments. Comparison of results from columns operated with and without free chlorine, would help to clarify if an oxidation process of the adsorbed Mn (II) was always occurring, regardless of an oxidant feed. Data presented in Figures 32-36 show overlay plots of the release of Mn (II) back into solution for columns operated in the presence and absence of free chlorine, with Figure 33 representing the effluent pH pattern for media #2 during this pH 5.0 backtitration. Note that in these particular figures, a scale change has been made in the x-axis (volume filtered) to help clarify any trends in the data. Curves representing those columns operated without chlorine being present during Mn (II) uptake show a strong

TABLE 6: KMnO_4 Demands by Oxide-Coated Filter Media Exerted during Mn^{2+} Removal in the Presence and Absence of 2 mg/L HOCl (expressed in meq)

MEDIA SAMPLE #	INFLUENT pH	<u>NO HOCl PRESENT</u>		<u>HOCl PRESENT</u>		
		Mn ²⁺ UPTAKE	$\frac{\text{KMnO}_4}{\text{DEMAND}}$	Mn ²⁺ UPTAKE	$\frac{\text{KMnO}_4}{\text{DEMAND}}$	HOCl DEMAND
1 (3 mg/g)	6-6.2	0.30	0.42	3.20	0.73	1.73
	7.8	1.09	1.25	6.50	0.72	7.50
	8.8	2.80	1.69	----	----	----
2 (4 mg/g)	6-6.2	0.60	0.87	4.15	0.79	4.40
	7.8	0.99	1.16	3.10	0.24	2.80
	8.8	1.94	0.66	1.70	0.29	1.78
3 (14 mg/L)	6-6.2	1.53	1.12	7.36	1.36	5.75
	7.8	3.00	1.54	7.80	0.80	9.10
4 (42 mg/g)	6-6.2	14.1	11.9	10.7*	3.30	10.3
	7.8	13.3	13.4	----	----	----

* Study completed; column without HOCl continued

Table 7. Extended Free Chlorine Feed and Subsequent KMnO_4 Demand for Oxide-Coated Filter Media #1 at pH 6-6.2 (expressed in meq)

Mn (II) UPTAKE w/HOCl	HOCl DEMAND	EXTENDED HOCl DEMAND	KMnO_4 DEMAND. w/HOCl
7.07	4.93	1.24	0.30

initial peak of Mn (II) being released back into solution. Effluent pH values were also monitored during experimentation and a greater rise in pH occurred for columns without free chlorine (see Figure 33). In comparison, columns operated with chlorine tended to have much lower effluent manganese concentrations throughout this release study. These results indicate that unless an oxidant such as free chlorine is present in the filter-applied water, the adsorbed Mn (II) will not be oxidized directly on the media surface. These results agree with the work of Morgan and Stumm (19) who concluded that no reaction between adsorbed Mn^{2+} and $\text{MnO}_{2(s)}$ occurred unless the pH was greater than 9.0.

Repeated Mn^{2+} Uptake Studies with KMnO_4 and HOCl Regeneration

One particular media [media #2; (4 mg/g) surface Mn (II) concentration] was investigated for its regeneration capacity using KMnO_4 and HOCl to oxidize the adsorbed Mn^{2+} on the oxide-coated media. A repetitive Mn^{2+} uptake study in the absence of free chlorine was performed on this media at pH 7.8. As the column began to fail during the first uptake study, a 100 mg/L KMnO_4 regeneration on the exhausted media was performed. Following the KMnO_4 demand of the oxide-coated media, a second Mn^{2+} uptake study was conducted. Again following media exhaustion, a final KMnO_4 of the oxide-coating was performed. The data presented in Figure 37 show the results of repeated Mn^{2+} uptake studies conducted at pH 7.8 with influent manganese concentrations maintained at 1.0 mg/L. In the following figure (see Figure 38), the results from the KMnO_4 demand of the exhausted media are plotted. Oxidation of the adsorbed Mn^{2+} upon the oxide-coated surface by the 100 mg/L KMnO_4 feed resulted in additional $\text{MnO}_{2(s)}$ being precipitated directly on the media surface. This lead to a greater amount of Mn^{2+} uptake during the second study (refer to Figure 37) due to additional sites for adsorption upon the oxide surface. The results from these experiments and subsequent studies to be addressed next are summarized into Table 8.

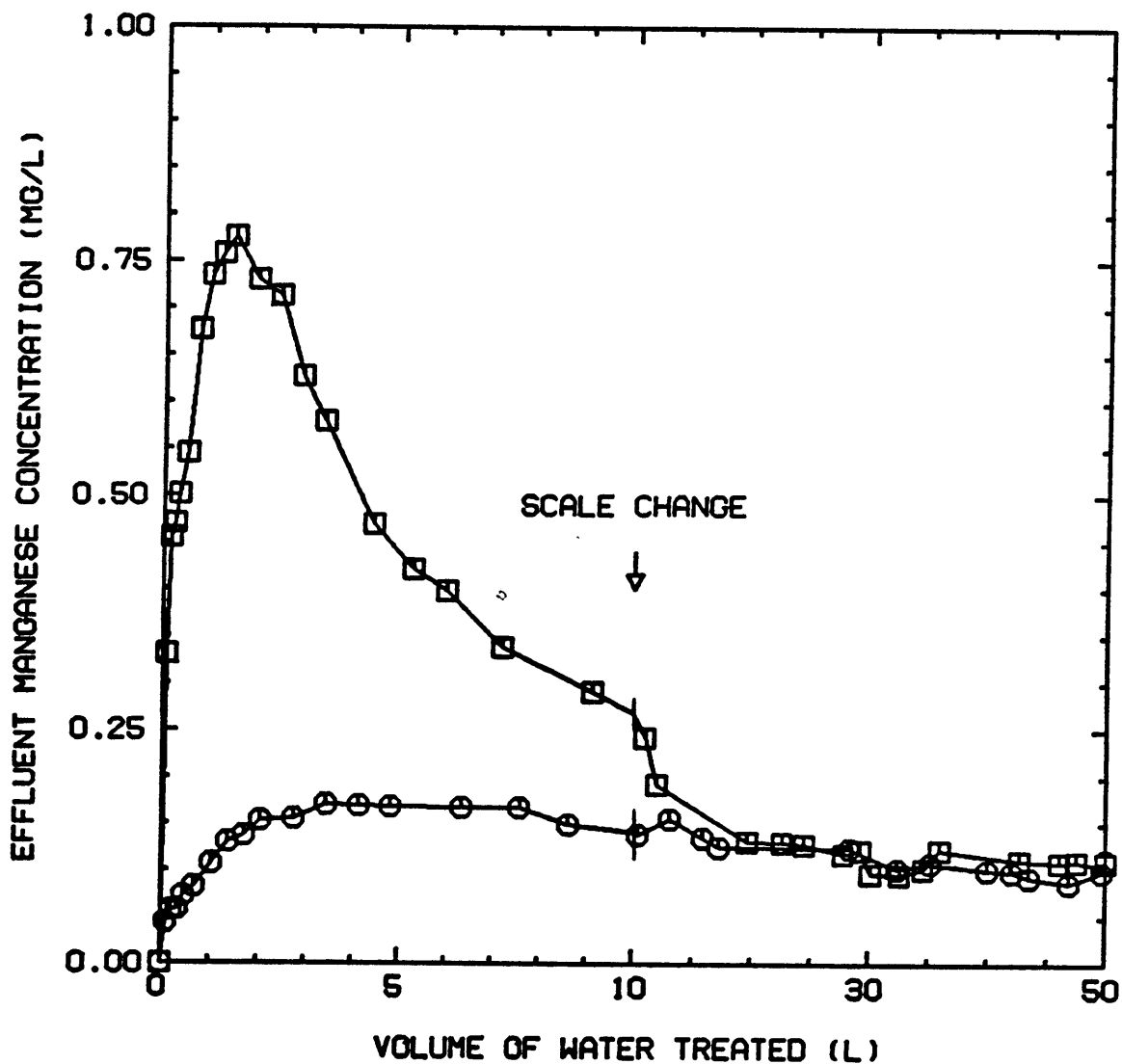


Figure 32. Release of Mn^{2+} From Oxide-Coated Filter Media During Exposure to pH 5.0 Conditions: [Media #2; initially operated for Mn^{2+} removal at pH 6-6.2 in the presence (○) and absence (□) of HOCl]

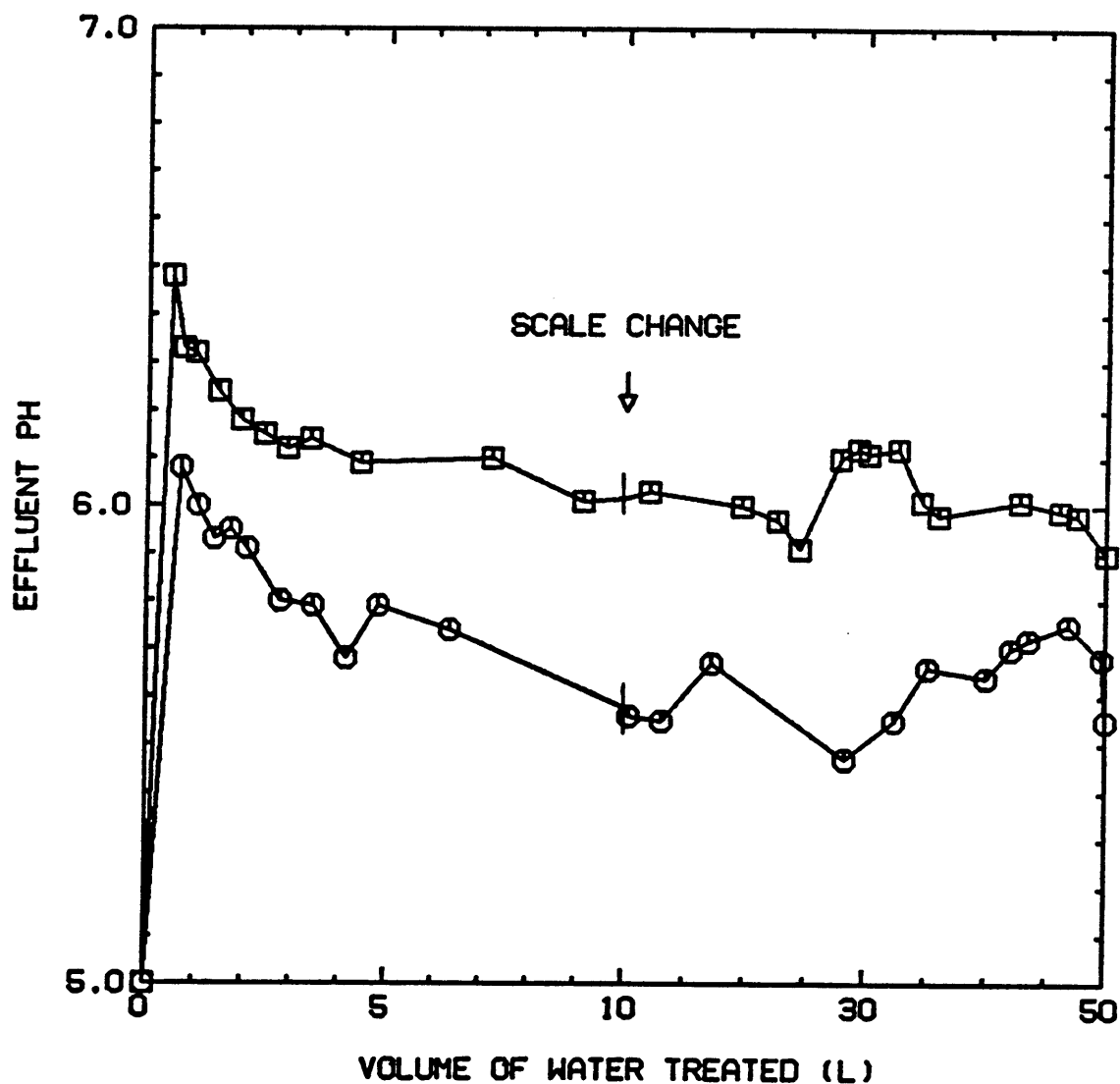


Figure 33. Effluent pH during Exposure to pH 5.0 Conditions on Oxide-Coated Filter Media: [Media #2; initially operated for Mn^{2+} removal at pH 6-6.2 in the presence (○) and absence (□) of HOCl]

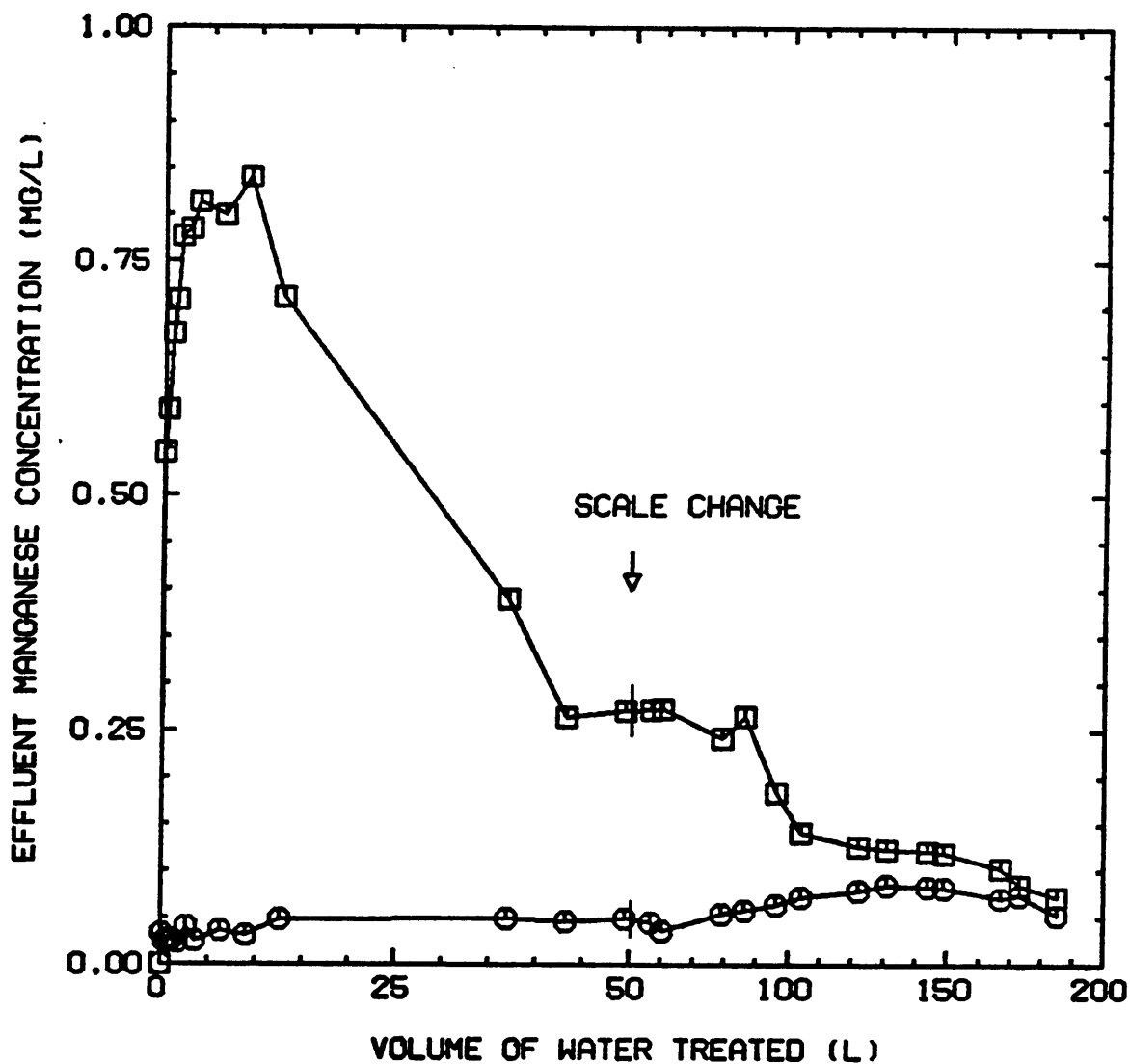


Figure 34. Release of Mn^{2+} From Oxide-Coated Filter Media During Exposure to pH 5.0 Conditions: [Media #3; initially operated for Mn^{2+} removal at pH 6-6.2 in the presence (○) and absence (□) of HOCl]

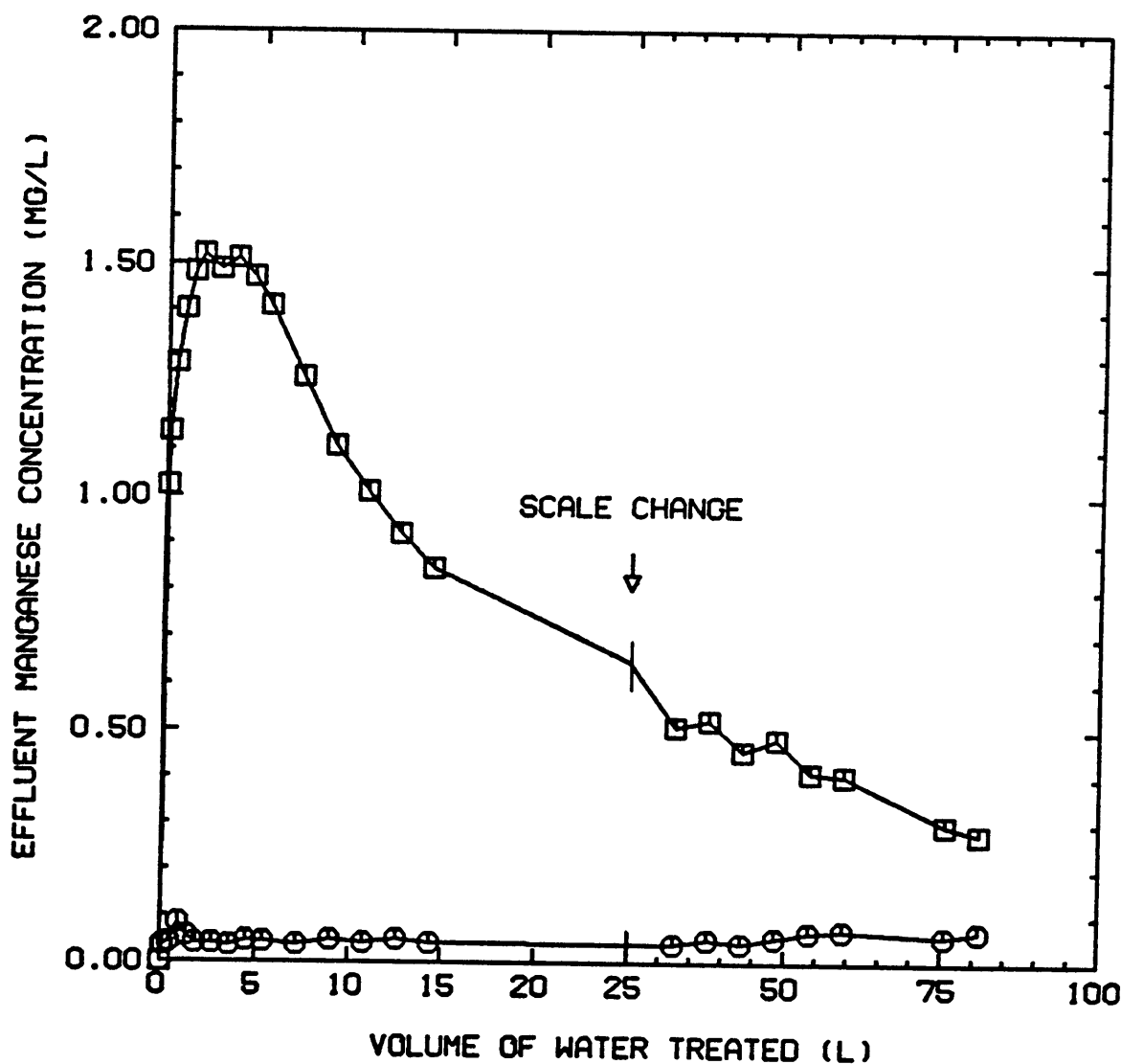


Figure 35. Release of Mn^{2+} From Oxide-Coated Filter Media During Exposure to pH 5.0 Conditions: [Media #3; initially operated for Mn^{2+} removal at pH 7.8 in the presence (○) and absence (□) of HOCl]

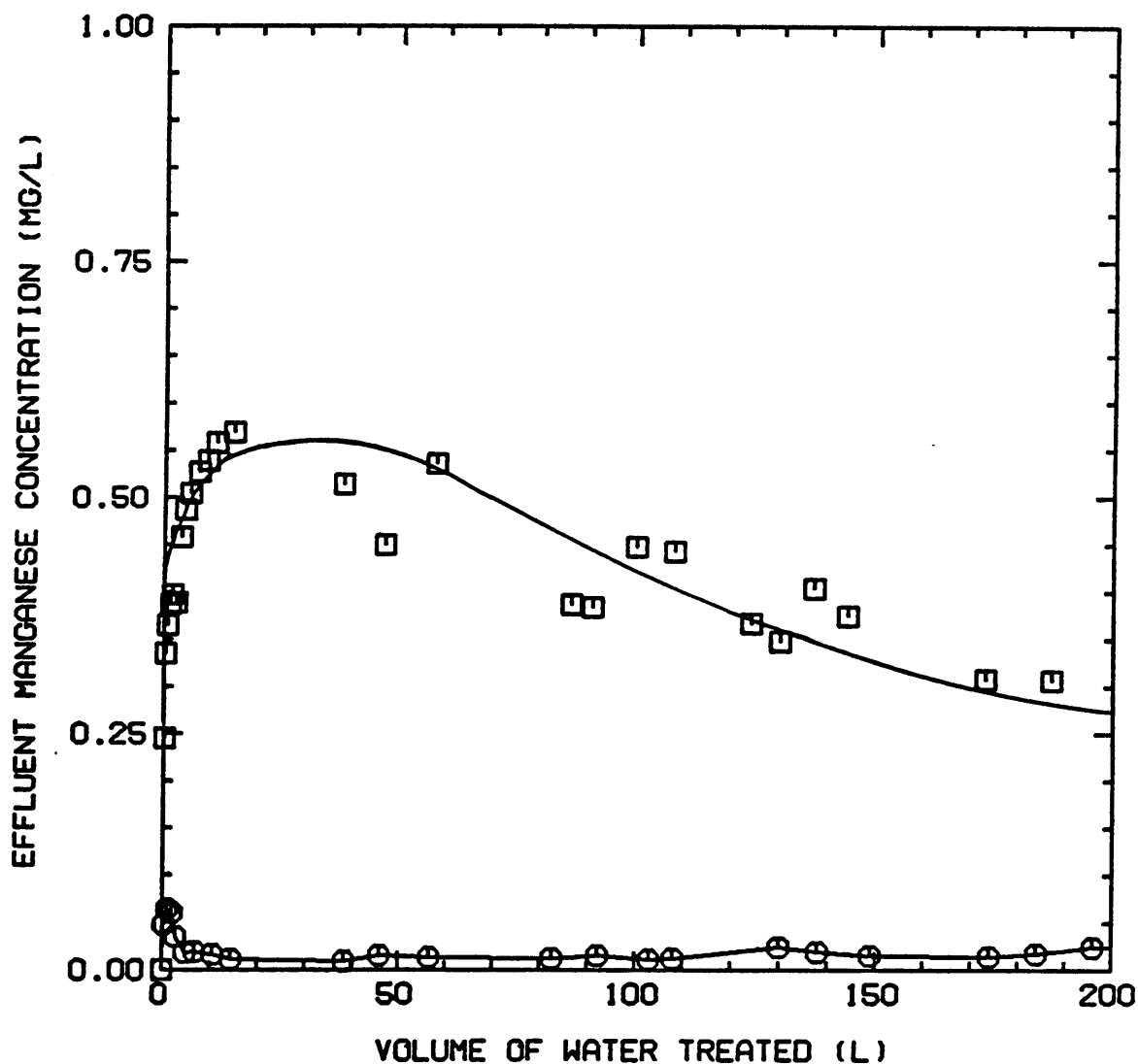


Figure 36. Release of Mn^{2+} From Oxide-Coated Filter Media During Exposure to pH 5.0 Conditions: [Media #4; initially operated for Mn^{2+} removal at pH 6-6.2 in the presence (○) and absence (□) of HOCl]

Following regeneration of exhausted media using KMnO_4 , the possibility of utilizing free chlorine for regeneration during backwashing was investigated due to its inexpensiveness. The studies with free chlorine were conducted in a similar manner as in the previous experiments utilizing KMnO_4 . However, instead of only two Mn^{2+} uptake studies, a third and final exhaustion study was performed. Rather than employing the more costly KMnO_4 , a 50 mg/L HOCl solution was fed to the columns to oxidize the adsorbed Mn^{2+} following depletion of adsorption sites upon the oxide coating. The HOCl demand of the oxide-coated filter media was conducted after each of the three Mn^{2+} uptake studies. The three Mn^{2+} breakthrough curves during these studies utilizing HOCl to regenerate the media are presented in Figure 39. Data from the three HOCl demands of the adsorbed Mn^{2+} are plotted in Figure 40. From data generated from these final experiments (refer to Figures 39 and 40), it is possible to recover the removal capacity of the oxide-coating for media #2 using free chlorine. Table 8 again summarizes data from the KMnO_4 and HOCl regeneration of repeated Mn^{2+} uptake studies. These preliminary results indicate that chlorine may be used as a viable alternative to KMnO_4 for the regeneration of oxide-coated filter media. However, further experiments on the effects of surface oxide concentration on the media and pH influences are still needed.

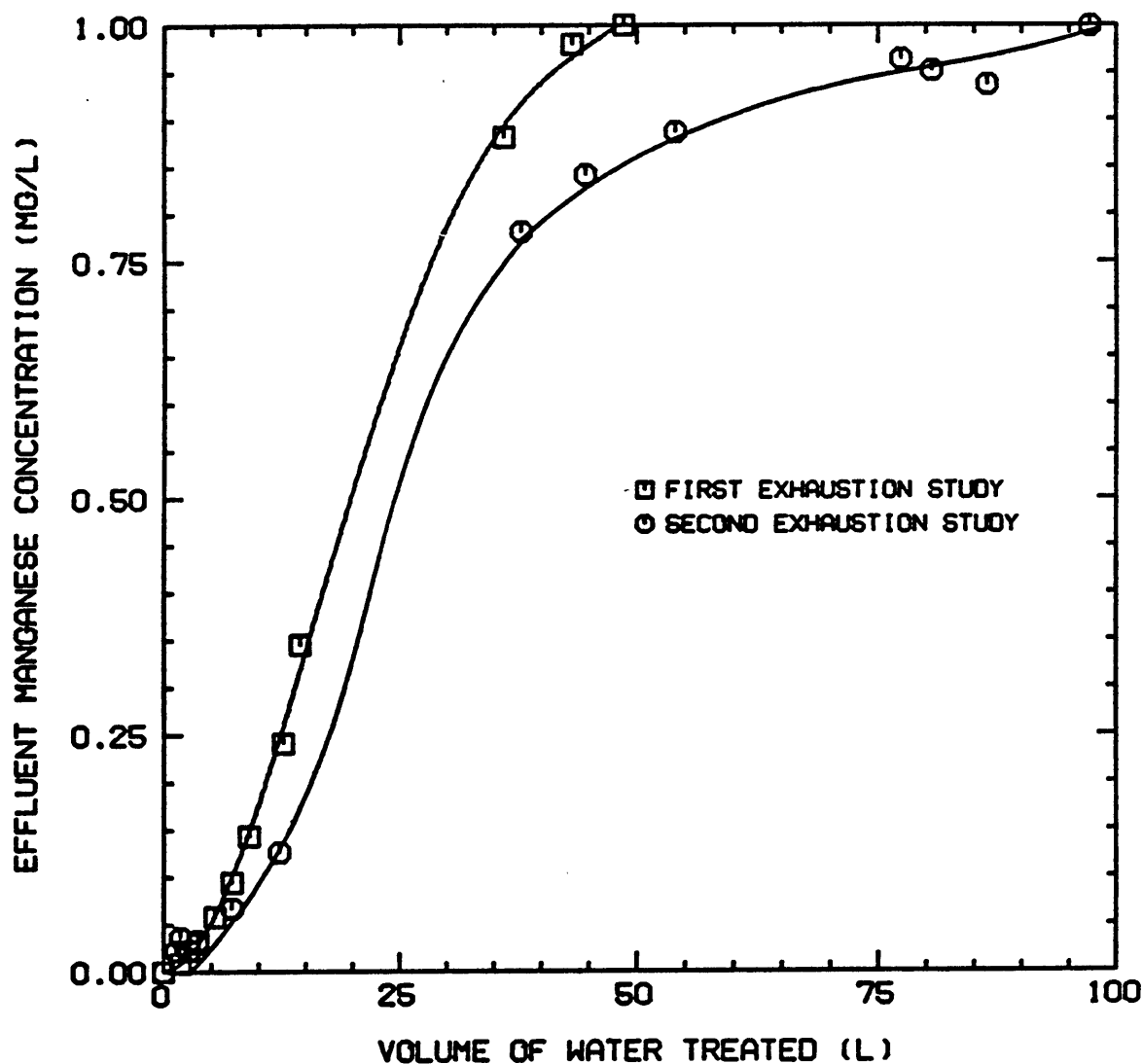


Figure 37. Repeated Mn^{2+} Uptake Studies Conducted at pH 7.8 with KMnO_4 Regeneration of Exhausted Oxide-Coated Filter Media: [Media #2; surface extracted concentration (4 mg/g); Influent Mn (II) = 1.0 mg/L]

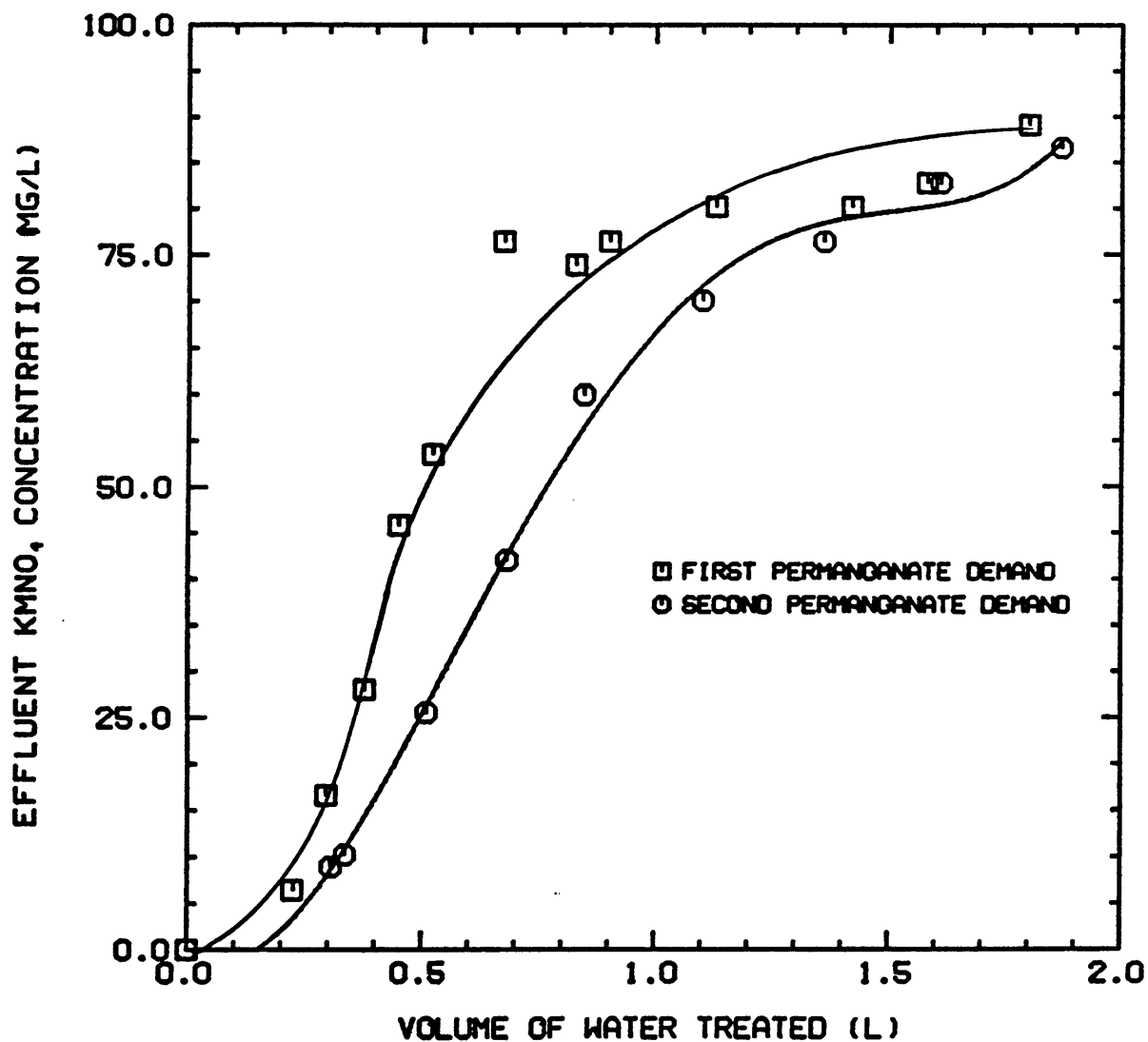


Figure 38. Repeated KMnO_4 Regeneration of Exhausted Oxide-Coated Filter Media: [Media #2; surface extracted concentration (4 mg/g); Influent KMnO_4 = 100 mg/L]

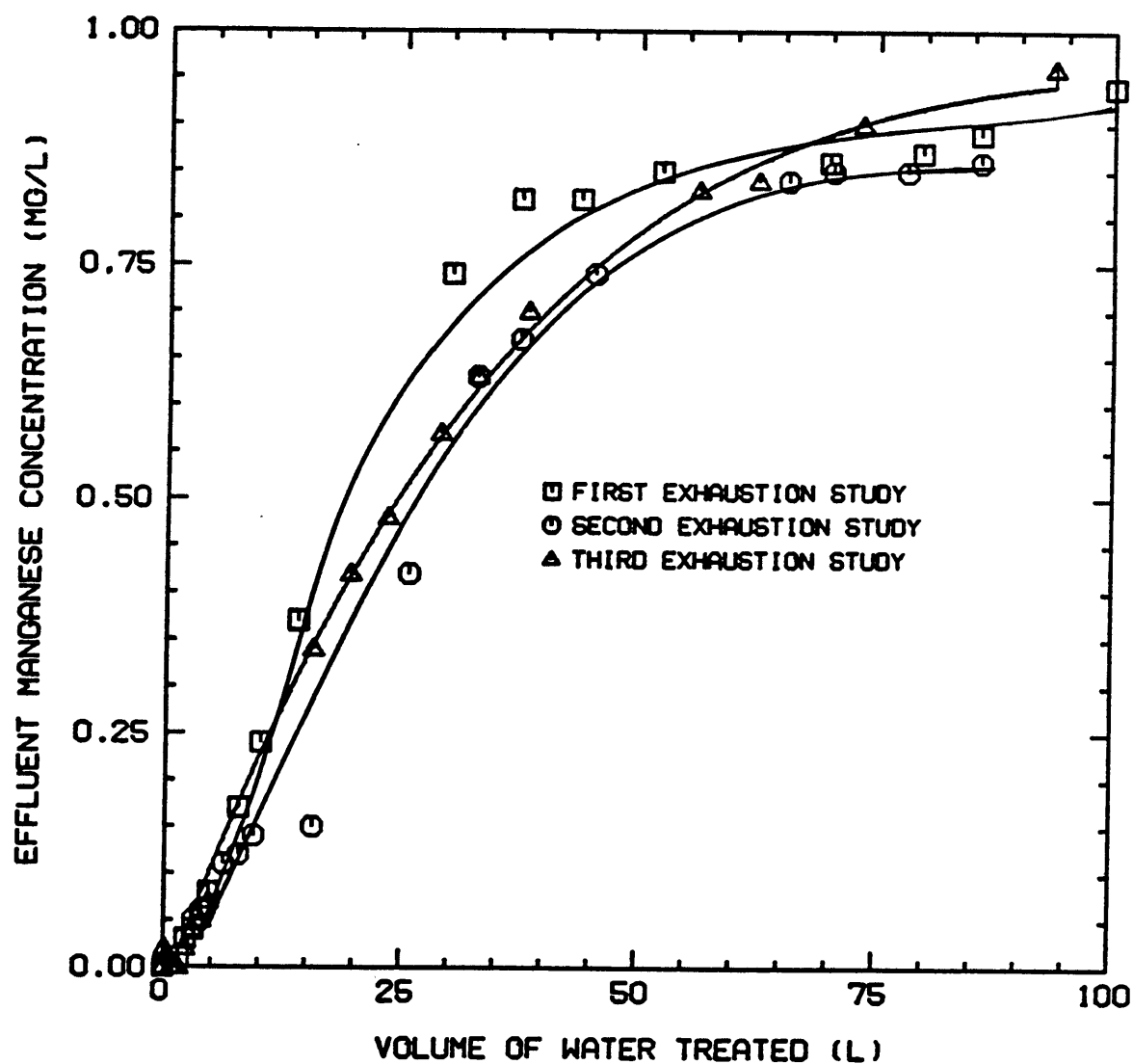


Figure 39. Repeated Mn^{2+} Uptake Studies Conducted at pH 7.8 with HOCl Regeneration of Exhausted Oxide-Coated Filter Media: [Media #2; surface extracted concentration (4 mg/g); Influent Mn (II) = 1.0 mg/L]

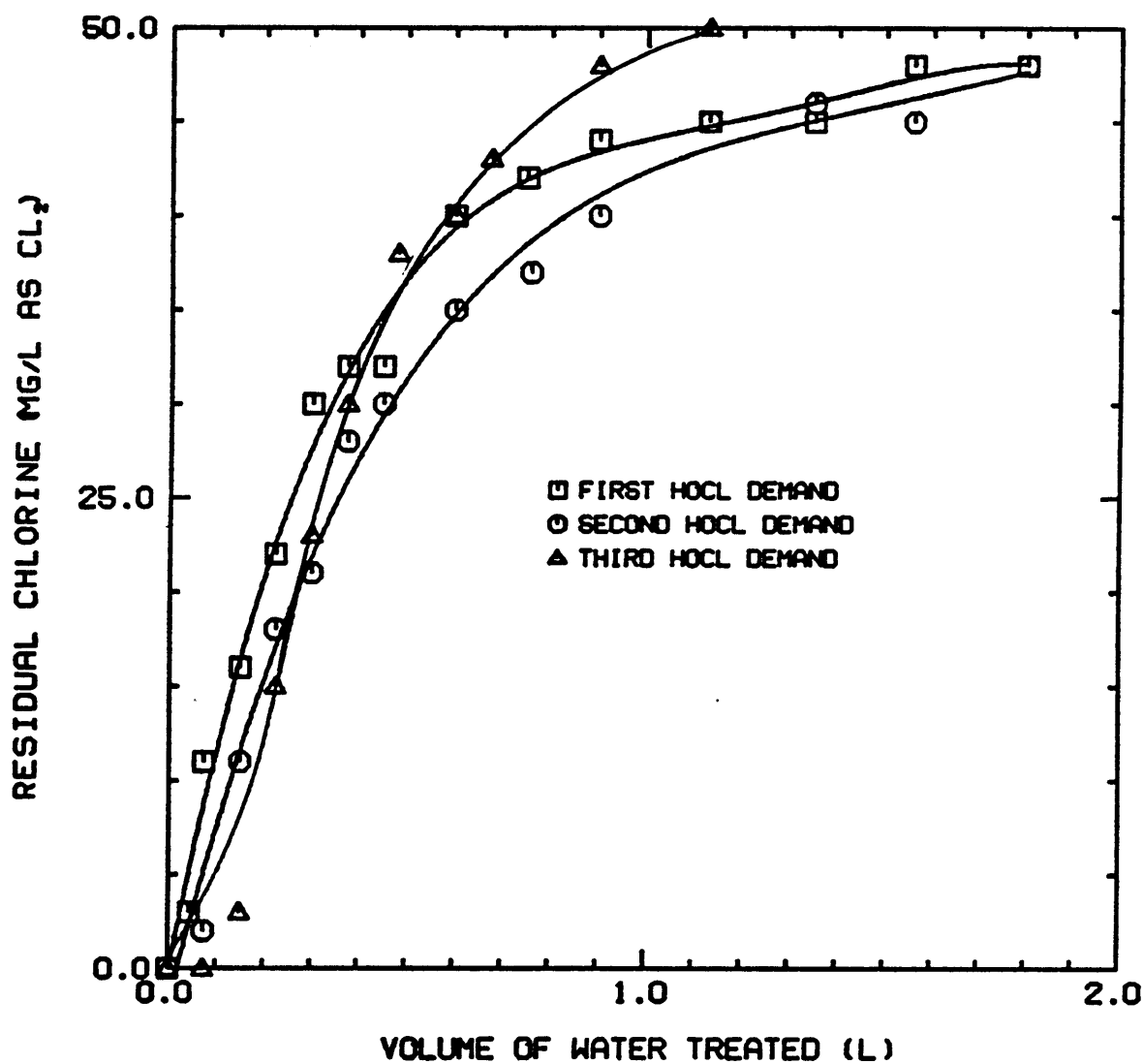


Figure 40. Repeated HOCl Regeneration of Exhausted Oxide-Coated Filter Media: [Media #2; surface extracted concentration (4 mg/g); Influent KMnO_4 = 100 mg/L]

Table 8. Repetitive Mn (II) Uptake Studies for Media #2 at pH 7.8 in the Absence of Free Chlorine (expressed in meq)

	Mn (II) UPTAKE w/HOCl	KMnO ₄ DEMAND	HOCl DEMAND
1ST EXHAUSTION	0.79	0.96	---
2ND EXHAUSTION	1.18	1.25	---
1ST EXHAUSTION	1.05	---	0.60
2ND EXHAUSTION	1.44	---	0.74
3RD EXHAUSTION	1.42	---	0.55

DISCUSSION

Experimental results are further explained in the following section. This chapter presents a detailed discussion into the results of the previous section and is organized into similar subsections: Mn (II) removal studies, KMnO_4 demands of oxide-coated filter media, release of Mn^{2+} from the oxide-coated filter media and repeated Mn^{2+} uptake studies using KMnO_4 or HOCl for regeneration of the exhausted media. A summary of most of the research results has been provided in Table 9.

Mn (II) Removal Studies

Many factors can affect the uptake of soluble manganese by oxide-coated filter media. Three parameters were extensively researched during this project: surface oxide concentration, solution pH and oxidant effects.

Characterization of Water Treatment Plant Filter Media

The manganese oxide coating present on each of the media samples had a vital role in the uptake of soluble manganese. By solubilizing the manganese coating with a strong reducing agent, (HAS), the amount of oxide coating upon the filter media surface could be quantified (see Table 2). Four different media of varying amounts of oxide coating were investigated. Following a 2% KMnO_4 regeneration of the media to completely oxidize the surface coating to manganese dioxide ($\text{MnO}_{2(s)}$), the HAS extractions were

TABLE 9: HOCl and KMnO₄ Demands Exerted during Mn²⁺ Removal in the Presence and Absence of 2 mg/L HOCl; Mn (II) Release Data (expressed in mcq)

MEDIA SAMPLE #	INFLUENT pH	Mn ²⁺ UPTAKE	Mn ²⁺ RELEASE	AMT. RELEASED	HOCl DEMAND	KMnO ₄ DEMAND
1 w/o HOCl	6-6.2	0.30	1.80	600%	----	0.42
w/ HOCl		3.20	----	----	1.73	0.73
w/o HOCl	7.8	1.09	1.79	164%	----	1.25
w/ HOCl		6.50	1.26	19.4%	7.50	0.72
w/o HOCl	8.8	2.80	1.90	67.9%	----	1.69
w/ HOCl		----	----	----	----	----
2 w/o HOCl	6-6.2	0.60	0.40	66.7%	----	0.87
w/ HOCl		4.15	0.34	8.20%	4.40	0.79
w/o HOCl	7.8	0.99	----	----	----	1.16
w/ HOCl		3.10	----	----	2.80	0.24
w/o HOCl	8.8	1.94	----	----	1.78	0.66
w/ HOCl		1.70	----	----	1.78	0.29
3 w/o HOCl	6-6.2	1.53	1.79	117%	----	1.12
w/ HOCl		7.36	0.41	5.57%	5.75	1.36
w/o HOCl	7.8	3.00	1.30	60.0%	----	1.54
w/ HOCl		7.80	0.15	1.90%	9.10	0.82
4 w/o HOCl	6-6.2	14.1	3.75	26.6%	----	11.9
w/ HOCl		10.7*	0.15	1.40%	10.3	3.30
w/o HOCl	7.8	13.3	4.00	30.0	----	13.4
w/ HOCl		----	----	----	----	----

*Study completed; column without HOCl continued

performed. Similar amounts of oxide coating were present on media #1 and #2; samples of media #3 and #4 were included to investigate the effects of larger amounts of surface oxide coating upon Mn (II) removal.

The manganese oxide coating on the media surface acts as a surface catalyst and an adsorption site for manganese. The results from previous work by Palmer (30) indicated that the amount of oxide coating as well as the oxidation state of the $\text{MnO}_{x(s)}$ are crucial parameters for effective Mn (II) removal. That is, Mn (II) removal efficiency is greatly enhanced by having the surface coating fully oxidized. In this study, this was accomplished by a 2% KMnO_4 regeneration prior to use of the media in the Mn (II) removal studies. In its fully oxidized state, the media surface would be expressed as a manganese dioxide ($\text{MnO}_{2(s)}$) coating. As soluble Mn (II) sorbs to this $\text{MnO}_{2(s)}$ coating, the sites for adsorption begin to decrease. Saturation of adsorption sites leads to Mn (II) breakthrough and eventual exhaustion of the oxide-coated filter media. The term often used to describe this type of Mn (II) removal mechanism occurring in dual-media filters is referred to as the "natural greensand effect" (2). In the absence of an oxidant, the media's natural greensand process begins to fail and the media must be regenerated to yield new adsorption sites.

Following extraction experiments to quantify the amount of oxide coating present in its fully oxidized state, column studies were conducted in the absence and presence of a continuous feed of free chlorine. Two parameters under consideration during this testing were media and pH effects.

Removal of Mn (II) in the Absence of Free Chlorine

Results obtained from column studies in the absence of free chlorine are first discussed. Dechlorinated Blacksburg, Virginia tap water containing 1.0 mg/L Mn^{2+} was filtered

through media-packed columns. Also serving as the "control", these column studies could be compared with columns operated with a continuous feed of an oxidant. The influence of surface oxide concentration and pH effects were emphasized in this particular phase of the study.

Effects of Surface Oxide Coating and Solution pH on Adsorption Capacity

Data on the influences of surface oxide coating and solution pH on the removal of Mn (II) have been presented in Figures 11-17. Table 3 summarized the amount of Mn (II) uptake in relation to the amount of surface oxide coating and influent pH. An increase in both oxide coating concentration and solution pH resulted in greater capacity for Mn (II) uptake due to the availability of more adsorption sites.

Hydrous Mn oxides presented in a microcrystalline form are characterized by high specific surface areas up to 300 m²/g for MnO₂. The sorption of Mn (II) to manganese oxides have been interpreted by Morgan and Stumm (10) as a surface complexation and/or ion exchange process where hydrogen ions or other cations are released as Mn²⁺ is adsorbed. Transition and heavy metal ions become specifically attached to the surface. This adsorption process is strongly dependent upon solution pH (See Figure 2). (10)

In this study, adsorption of Mn (II) on the oxide coating was also highly pH dependent with Mn (II) uptake increasing at higher pH conditions. One explanation for this mechanism is that as the influent pH increased, additional sites for Mn²⁺ adsorption were made available due to the release of H⁺ ions from such sites. The largest oxide-coated media [media #4; 42 mg Mn (II)/g media] at pH 6-6.2 and 7.8 had tremendous capacity for Mn (II) removal even in the absence of an oxidant due to increased availability of adsorption sites [refer to Figure 17 (note scale change of y-axis)].

Morgan and Stumm (19) showed that the net surface charge of $\text{MnO}_{2(s)}$ became more negative as solution pH increased, indicating that the number of adsorption sites available per unit weight of $\text{MnO}_{2(s)}$ also would increase. During the present study, attempts were not made to directly determine the surface charge density of the oxide-coated media. However, inferences regarding the impact that the number of available adsorption sites can be developed.

Consider the Mn (II) breakthrough curves plotted in Figure 41 for two column studies, each receiving a 1.0 mg/L Mn (II) feed solution without HOCl present. One column had a higher manganese oxide surface concentration (14 mg/g as Mn) and was operated at pH 6-6.2. The second column had a lower manganese oxide surface concentration (3 mg/g as Mn) but was operated at a higher pH condition. The pH 7.8 system would have produced a greater specific number of adsorption sites when considering the number of negative sites per unit weight of manganese oxide. Thus, it was hypothesized that these combinations of surface oxide concentrations and operating pH conditions may have produced two columns for manganese removal with similar numbers of available adsorption sites. The breakthrough curves show that the capacity of these two columns for manganese removal is indeed similar, supporting the hypothesis that the number of available adsorption sites has a key role in defining the Mn (II) removal capacity of manganese oxide coatings.

The surface, oxide coating concentration of the filter media and influent pH greatly influenced the removal mechanisms of soluble manganese. In the absence of free chlorine, exhaustion of the filter media was observed due to the decreased capacity of the oxide coating to adsorb additional Mn^{2+} . Calculation of the KMnO_4 demand of the oxide coating following filter media exhaustion showed that the KMnO_4 requirement for me-

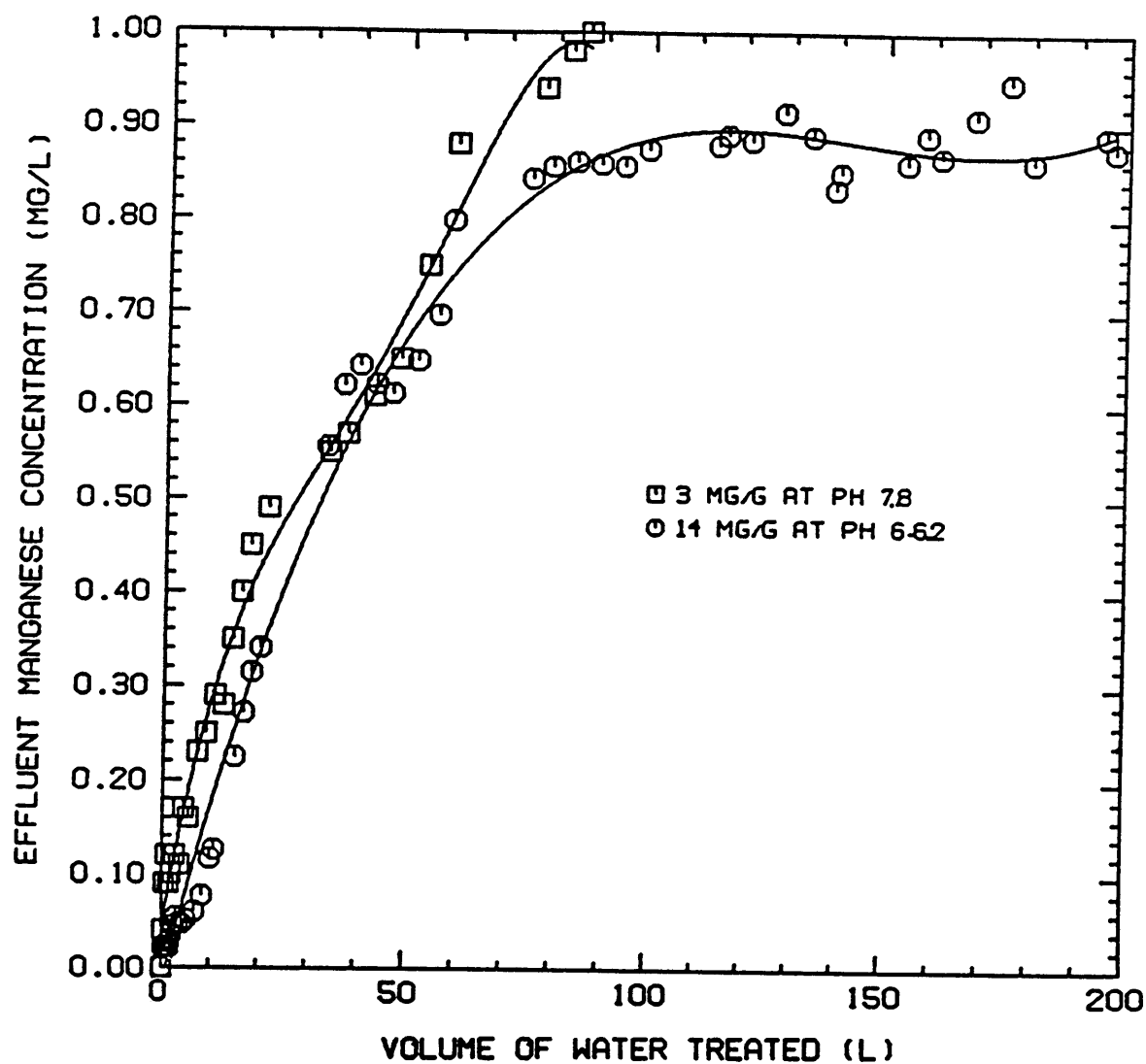


Figure 41. Surface Oxide Concentration and Solution pH Effects upon the Removal of Mn (II) in the Absence of HOCl: [Mn (II) Influent = 1.0 mg/L]

dia regeneration was reasonably equivalent to the amount of Mn^{2+} uptake observed (refer to Table 9 for comparison). This result is not necessarily surprising since the Mn (II) removed was the only oxidant demand applied to the filter column. However, the question concerning auto-oxidation of the adsorbed Mn^{2+} by the $\text{MnO}_{x(s)}$ coating was yet to be answered. Was the KMnO_4 regeneration oxidizing only the adsorbed Mn^{2+} or was the demand for KMnO_4 being attributed to a reduced oxide coating (MnOOH) that had been reduced during the auto-oxidation of the adsorbed Mn^{2+} ?

To help answer the question concerning the mechanisms responsible for removing Mn^{2+} on oxide-coated filter media, a pH 5.0 backtitration was performed following completion of column operations. The release data at pH 5.0 in the absence of HOCl showed significant amounts of Mn (II) were desorbed ($> 70\%$; refer to Table 9). This implied that Mn^{2+} was adsorbed but never oxidized by the oxide coating. These results refute Weng *et al.* (18) who concluded that the oxide surface did auto-oxidize the Mn^{2+} with the concurrent reduction of the oxide surface. If this auto-oxidation process was occurring, the exposure to pH 5.0 conditions would not have yielded the release of Mn^{2+} back into solution. This conclusion is supported by Morgan and Stumm (19) who found no evidence of auto-oxidation of Mn^{2+} by the oxide surface in the absence of an oxidant when the solution pH was less than 9.0.

In summary, surface adsorption appears to be the mechanism responsible for Mn^{2+} removal by oxide-coated filter media in the absence of an oxidant. The results of the pH 5.0 titration of the oxide-coated media also point to a potential problem in water treatment operations. A decrease in the pH of the filter-applied water would theoretically produce a corresponding reduction in the specific surface concentration of adsorption sites available on the oxide coating. Such a reduction in sites could lead to the possible

desorption of previously adsorbed Mn^{2+} as H^+ ions replace the manganese ions. This release, occurring at the end of the water treatment process would result in elevated soluble manganese concentrations leaving the plant.

Column studies for Mn (II) desorption were only conducted at pH 5.0, so there is no direct desorption data to support this hypothesis. However, column studies did indicate that the Mn (II) adsorption capacity of each media sample decreased as the solution pH decreased. Such results would give credence to the possibility that a reduction in the pH of the filter-applied water may lead to Mn (II) desorption.

Mn (II) Removal in the Presence of Free Chlorine

The presence of free chlorine promoted the efficient removal of soluble manganese across the oxide-coated filter media for extended periods of column operation. There was no evidence of significant column exhaustion occurring, even when operating under pH 6-6.2 conditions (refer to Figures 22-26; results are summarized in Table 9).

The question to be addressed was ascertaining the exact role of free chlorine in promoting the long-term manganese removal capacity of the filter media. One possibility was that free chlorine was oxidizing the Mn (II) between the time that HOCl was added to the water and the water actually reached the filter media. However, water samples collected just prior to the top of the filter column showed no indication of manganese oxidation. Further, Knocke *et al.* (2) determined that free chlorine was very inefficient for manganese oxidation unless the solution pH was above 8.0-8.5. Instead, it was hypothesized that HOCl was oxidizing previously adsorbed Mn (II) on the oxide surface, with the surface serving as a catalyst for the oxidation reaction. This hypothesis is supported by considering the HOCl demand versus Mn (II) uptake data presented in

Table 9 for several column studies. These results showed a reasonably close correlation between these two parameters when considered on an equivalence basis.

Previous work by Knocke *et al.* (3) also considered the role of free chlorine in such systems under higher influent HOCl situations where the observed HOCl demand was above the stoichiometric requirements, free chlorine was thought to be reacting to regenerate the oxidation state of the $\text{MnO}_{x(s)}$ surface coating. In situations where chlorine consumption was less the stoichiometric amount, the complete removal of Mn^{2+} indicated that sorptive removal capacity of the filter was contributing to overall Mn (II) removal. The authors also noted that the presence of significant free chlorine ($> 1\text{-}2 \text{ mg/L as Cl}_2$) promoted rapid, continuous uptake of soluble manganese within oxide-coated filters. (3)

The role of HOCl in maintaining the viability of oxide surfaces for manganese removal may also be seen through data included in Figure 42. In this figure, the manganese breakthrough graphs are plotted for the same column configurations presented in Figure 41 (media #1 at pH 7.8; media #3 at pH 6-6.2). However, in these side-by-side column studies, HOCl is present in the filter-applied water. The interpretation of Figure 42 is that these sites are continually regenerated since the effluent Mn (II) concentration remains fairly constant for both columns. Thus, HOCl must be functioning to oxidize previously adsorbed manganese ions.

Continuous regeneration of the oxide coating by HOCl has also been observed at the Williams Water Treatment Plant in Durham, North Carolina (33). This facility ceased prechlorination of its raw water in 1976 due to concerns related to the formation of chlorinated organics. The point of chlorine addition was moved to just prior to the filters; no other oxidants are routinely added to the water. Monitoring Mn^{2+} concen-

trations following filtration at the plant had indicated that HOCl addition prior to the oxide-coated filters has consistently produced effluent manganese concentrations below 0.01 mg/L, even when treating waters with soluble manganese concentrations above 0.05 mg/L. It should be noted that media #4 used during this research study was in fact collected from the Williams Water Treatment Plant.

The demand for KMnO_4 in the presence of 2 mg/L HOCl was attributed to the Mn^{2+} sorbed just prior to stopping the column. The contact time with the HOCl was not long enough to oxidize the sorbed Mn^{2+} . The data from the extended HOCl study (see Table 7) resulted in a greatly reduced KMnO_4 demand of 0.30 meq compared to 1.73 meq for the column without the extended HOCl feed. This demonstrated the need for HOCl to fully regenerate the oxide coating during backwashing even though a continuous oxidant was being supplied.

The pH 5.0 backtitration studies in the presence of HOCl showed minimal Mn^{2+} release, again indicating that Mn^{2+} was being oxidized on the surface by the HOCl (see Table 9). Figures 32-35 presented data from exposure to these acidic conditions in the presence and absence of HOCl. Columns operated with HOCl had significantly less amount of sorbed manganese released back into solution during the pH adjustment. These results again indicated that in the presence of HOCl in the feedwater, the adsorbed Mn^{2+} was directly oxidized on the media surface by the HOCl. Utilizing this manganese, "greensand-like" removal mechanism, the oxide-coated filter media acted to initially provide sorption sites for Mn^{2+} and subsequently, aided in catalyzing the oxidation of Mn^{2+} to $\text{MnO}_{x(s)}$ by HOCl.

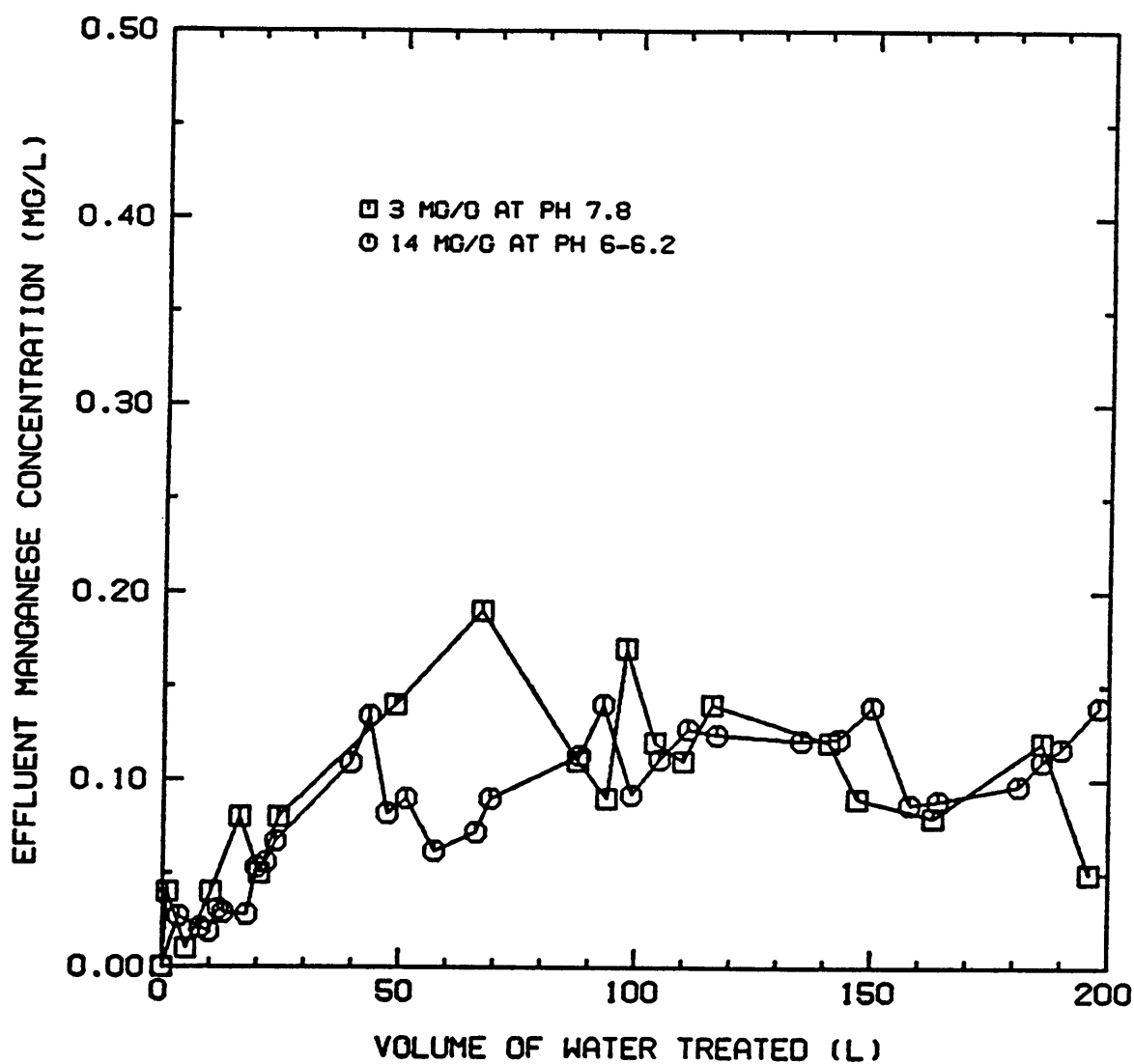


Figure 42. Surface Oxide Concentration and Solution pH Effects upon the Removal of Mn (II) in the Presence of 2 mg/L HOCl: [Mn (II) Influent = 1.0 mg/L]

Repeated Mn^{2+} Uptake Studies with KMnO_4 or HOCl Regeneration

The final area of research included a repetitive Mn^{2+} uptake study of oxide-coated filter media in the absence of free chlorine followed by KMnO_4 or HOCl regeneration. It was apparent from the data presented in Figure 37, the Mn^{2+} uptake capacity of the media increased during the second Mn^{2+} removal study. This is due to the fact that during KMnO_4 regeneration of the exhausted media, not only is the adsorbed Mn^{2+} being oxidized to $\text{MnO}_{2(s)}$ but the reduction of KMnO_4 is also contributing to additional $\text{MnO}_{2(s)}$ on the surface. This additional oxide coating allows for increased adsorption sites. The results presented in Table 8 and Figures 37 and 38 indicated that it was possible to recover all of the removal capacity of the oxide coating by KMnO_4 regeneration and additional Mn (II) removal was apparent after the second exhaustion/regeneration study.

Data on the use of free chlorine to regenerate exhausted filter media were presented in Figures 39 and 40. This testing included an additional exhaustion via Mn^{2+} uptake study and subsequent regeneration using HOCl . Results from these experiments indicated that free chlorine was also able to recover the removal capacity of the oxide-coating even after the third exhaustion study. Although there was a slight increase in the amount of Mn^{2+} removed during the second exhaustion study, the uptake capacity during the third exhaustion study remained the same. This is due to the fact that HOCl only oxidized the adsorbed Mn^{2+} to $\text{MnO}_{x(s)}$; unlike KMnO_4 , the reduction of HOCl did not contribute to additional $\text{MnO}_{2(s)}$. However, it was possible to recover the removal capacity of the oxide coating after three exhaustion studies with no loss of Mn (II) uptake capacity observed.

Extractions of the media were conducted following each exhaustion and HOCl regeneration cycles; results are presented in Table 10. The amount of surface oxide concentration increased after each exhaustion study due to additional $\text{MnO}_{(s)}$ on the surface from the HOCl oxidation of the adsorbed Mn^{2+} . From the experiments conducted, it would appear that HOCl can be used as a viable alternative to KMnO_4 for regeneration of oxide-coated filter media during backwashing. The concentration of HOCl needed to achieve such regeneration during a typical backwash cycle would be site specific.

Table 10. Amount of Extracted Manganese after Repeated Mn^{2+} Uptake Studies with HOCl Regeneration of Exhausted Media (expressed in mg Mn/g of media)

MEDIA SAMPLE #	INITIAL Mn CONC (mg/g)	FIRST EXHAUSTION	SECOND EXHAUSTION	THIRD EXHAUSTION
2	3.37	3.53	4.15	5.05

Note: [Influent Mn (II) = 1.0 mg/L; Operational pH 7.8]

CONCLUSIONS

To investigate more efficient techniques for soluble manganese removal, continuous-flow columns were operated in the presence and absence of free chlorine. Characterization of four different water treatment plant filter media for their Mn^{2+} removal capacity, KMnO_4 demands of the oxide-coated filter media and studies on the release of Mn^{2+} from the oxide surface were conducted. In addition, KMnO_4 and HOCl regenerations of exhausted media were undertaken. Based on these results and discussion of the accumulated data, the following conclusions were reached:

1. The amount of soluble manganese uptake on oxide-coated filter media is dependent upon the $\text{MnO}_{x(s)}$ surface coating and the extent of its oxidation state on the filter media.
2. Soluble manganese removal efficiency by oxide-coated filter media is also a function of the pH of the filter-applied water. The removal process can be significantly impeded by acidic pH conditions. Solution pH appears to define the specific concentration of adsorption sites on the oxide coating.
3. Continuous application of free chlorine to oxide-coated filter media results in soluble manganese being directly oxidized upon the $\text{MnO}_{x(s)}$ surface coating.

4. "Aged" filter media continuously regenerated with free chlorine can result in increased soluble manganese removal through adsorption and subsequent oxidation directly on the media surface.
5. Repetitive Mn^{2+} uptake studies indicate that free chlorine can be used to regenerate exhausted oxide-coated filter media.

In summary, the removal of soluble manganese using oxide-coated, dual-media filters can be greatly enhanced by the presence of an oxidant, free chlorine. This continuous, free chlorine regeneration would aid in maintaining filter, effluent manganese concentration below the SMCL of 0.05 mg/L and eliminate the constraints that operating in the auto-oxidative mode places upon the filter-applied pH water (30). The results of the repetitive column cycling studies indicate that strategies could be developed to maintain acceptable manganese removal capacity in oxide-coated filters while eliminating free chlorine from the filter-applied water. By using free chlorine for regeneration during backwashing operations only, reductions in the formation of chlorinated organic compounds could also be realized. This would be an important consideration for many water treatment facilities facing the need to control both manganese and chlorinated organic concentrations in their finished water.

REFERENCES

1. Wong, J. M., "Chlorination-Filtration for Iron and Manganese Removal." *Journal of the American Water Works Association.*, 76, 76-79 (1984).
2. Knocke, W. R., Hoehn, R. C., and Sinsabaugh, R. L., "Using Alternative Oxidants to Remove Dissolved Manganese From Waters Laden with Organics." *Journal of the American Water Works Association.*, 79, 75-79 (1987).
3. Knocke, W. R., Hamon, J. R., and Palmer, C. C., "Soluble Manganese Removal on Oxide-Coated Filter Media." *Journal of the American Water Works Association.*, 80, 65-70 (1988).
4. Trace Inorganic Substances Committee, "Committee Report: Research Needs for the Treatment of Iron and Manganese." *Journal of the American Water Works Association.*, 79, 119-122 (1987).
5. O'Connor, J. T., "Iron and Manganese." in *Water Quality and Treatment.*, Prepared and Published by the American Water Works Association (1971).
6. Griffin, A. E., "Significance and Removal of Manganese in Water Supplies." *Journal of the American Water Works Association.*, 52, 1326-1334 (1960).
7. Pourbaix, M., *Atlas of Electrochemical Equilibria in Aqueous Solutions.* Pergamon Press, New York (1966).
8. Montgomery, J. M., "Iron and Manganese Removal." in *Water Treatment Principles and Design.* John Wiley & Sons, Inc., New York, 339-342 (1985).
9. Morgan, J. J., "Chemistry of Aqueous Manganese II and IV." Ph.D Dissertation, Harvard University, Cambridge, MA (1964).
10. Stumm, W. and Morgan J. J., *Aquatic Chemistry*, 2nd ed., John Wiley & Sons, Inc., New York (1981).
11. Faust, S. D. and Aly O. M., "Removal of Inorganic Contaminants." in *Chemistry of Water Treatment.* Butterworth Publishers, MA, 483-493 (1983).
12. Morgan, J. J., "Chemical Equilibria and Kinetic Properties of Manganese in Natural Waters." in *Principles and Applications of Water Chemistry*, Edited by S.D. Faust and J.V. Hunter, John Wiley & Sons, Inc., New York, 561-624 (1967).
13. Ficek, K. J., "Potassium Permanganate for Iron and Manganese Removal and Taste and Odor Control." in *Water Treatment Plant Design for the Practicing Engineer*,

Edited by Robert L. Sanks, Ann Arbor Science Publishers, Ann Arbor, Mich. (1980).

14. White, G. C., "Chemistry of Chlorination." in *The Handbook of Chlorination*. 2nd edition, Van Nostrand Reinhold Co., New York, 182-210 (1972).
15. Sawyer, C. N., and McCarty P. L., "Residual Chlorine and Chlorine Demand." in *Chemistry for Environmental Engineering*. 3rd edition, McGraw-Hill Book Co., New York, 385-404 (1978).
16. Edwards, S. E. and McCall G. B., "Manganese Removal by Breakpoint Chlorination." *Water and Sewage Works.*, 93, 303-305 (1946).
17. Mathews, E. R., "Iron and Manganese Removal by Free Residual Chlorination." *Journal of the American Water Works Association.*, 39, 680-686 (1947).
18. Weng, C., Hoven, D. L., and Schwartz, B. J., "Ozonation: An Economic Choice for Water Treatment." *Journal of the American Water Works Association.*, 78, 83-89 (1986).
19. Morgan, J. J., and Stumm, W., "Colloid-Chemical Properties of Manganese Dioxide." *Journal of the American Water Works.*, 19, 347-359 (1964).
20. Carlson, M. A., "Oxidation of Trihalomethane-Precursors and Manganese (II) by Chlorine Dioxide and Permanganate", Doctoral Dissertation, Virginia Polytechnic Institute and State University (1988).
21. Viessman, W. and Hammer, M. J., *Water Supply and Pollution Control*, 4th Edition. Harper and Row Publishers, New York (1985).
22. Aieta, E. M. and Berg, J. D., "A Review of Chlorine Dioxide in Drinking Water Treatment." *Journal of the American Water Works Association.*, 78, 62-72 (1986).
23. Hair, D. H., "An Investigation of the Potassium Permanganate and Chlorine Dioxide During the Oxidation of Reduced Manganese", Masters Thesis, Virginia Polytechnic Institute and State University (1987).
24. Condie, L. W., "Toxicological Problems Associated with Chlorine Dioxide." *Journal of the American Water Works Association.*, 78, 73-77 (1986).
25. Legube, B., Lefebvre, E., Barbier J., Paillard, H. and Bourbigot, M. M., "Removal of Humic Substances and Manganese in Slightly Mineralized Water by Means of Iron Salts and Ozone." *Proceedings of the 1988 Annual Conference of the American Water Works Association*, Orlando, FL, 1343-1359 (1988).
26. American Water Works Association, "Iron and Manganese Removal." , *Water Treatment Plant Design*, Published by American Water Works Association, (1969).
27. Wilmarth, W. A., "Removal of Iron, Manganese and Sulfides." *Water Wastes Engineering.*, 5, 52-54 (1968).
28. Gaveland, A. and Heertjes, P. M., "Removal of Manganese from Groundwater by Heterogeneous Autocatalytic Oxidation", *Transactions of the Institute of Chemical Engineers.*, 53, 154-164 (1975).

29. Sayell, K. M. and Davis, R. R., "Removal of Iron and Manganese from Raw Water Supplies Using Manganese Greensand Zeolite." *Industrial Water Engineering.*, 12, 20-24 (1975).
30. Palmer, C. C., "Manganese Removal by Oxidation and Mixed-Media Filtration", Masters Thesis, Virginia Polytechnic Institute and State University (1986).
31. *Standard Methods for the Examination of Water and Wastewater*, 16th edition, APHA-AWWA-WPCF, (1985).
32. Weber, W. J., "Chemical Oxidation." in *Physicochemical Processes for Water Quality Control*. John Wiley & Sons, Inc., New York, 363-411 (1972).
33. Rolan, T., Private Communication, Dept. of Public Works, Durham, N.C. (1988).

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