

MANGANESE REMOVAL FROM WATER WITH SODIUM HYPOCHLORITE
AND OTHER CHEMICALS

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ABSTRACT

The presence of significant amounts of manganese in water can create several problems for the consumer such as taste problems, discoloration of industrial products, staining household fixtures with brown or black color. Therefore the water should be treated if it contains amounts exceeding the ones allowed. Most of the treatment methods of manganese removal depend on the oxidation of manganese.

The present work aims at investigating suitable criteria for manganese removal from water by studying the effect of adding calcium hydroxide, sodium hydroxide and hypochlorite. It also investigates the effect of aeration on this removal.

The study concluded that sodium hypochlorite with a concentration of 600 ppm Cl⁻ decreases the manganese concentration from 670 ppb to 20 ppb with a removal efficiency of 97.39% at pH 10.9 with the aid of aeration for 10 min. The aeration was found to be an effective mean to minimize the dose of hypochlorite to overcome the residual Na⁺ ions.

The increase of contact time of air up to 60 min reduces the manganese concentration with removal efficiency up to 81% with hypochlorite concentration 200 ppm Cl⁻, and the increase of chlorine dose up to 300 ppm Cl⁻ as sodium hypochlorite solution added to the water increases the removal efficiency to 98%.

1. INTRODUCTION

Heavy metals are present in abundance naturally and enter the water cycle through a variety of geochemical processes. Many metals are also added to water by human-induced activities. At excessive concentrations, soluble metal compounds may be deleterious to health and subsequent water use. More specifically, high concentration of heavy metals in water supplies are undesirable because of the potential adverse effects on the health of organisms, suitability of water for various purposes, longevity of water and sewer networks, and aesthetics of the environment [1], [2].

Certain metals in low concentration are not harmful, but traces are essential to good nutrition (for example cobalt, copper, iron, selenium, and zinc). Some metal salts, on the other hand, may be toxic. Taste, staining, and corrosion characteristics are also important considerations in the selection of a source of drinking water supply. For example, iron and manganese may stain fixtures, discolor laundry, cause a discoloration of industrial products such as paper, textiles and leather [3], [4]. Also these metals may interfere with industrial processes. In these circumstances, the water supply must be treated before use.

Because heavy metals can adversely affect water supplies, the regulatory agencies have limited the heavy metals discharged to surface streams even from industrial and municipal sources [5]. In Egypt, the environment law specifies that the maximum Mn limit in water is 1 ppm in order to allow discharge waste water in maritime environment [6].

Manganese is the least toxic among the essential trace elements and many animals can tolerate relatively high intakes of several hundreds to several thousands ppm, depending on species, provided that the other essential nutrients are presents in adequate amounts. Interference with iron metabolism, specifically hemoglobin formation is one of the first toxic effects noticed [7].

The following industrial activities produce manganese in its industrial effluents: Metallurgical industry, metal plating, alloying, foundries, glass ware industry, ceramic industry, porcelain industry, fertilizers manufacture, dye manufacture, paint manufacture, ink manufacture, match production, battery manufacture [8].

Methods in use for manganese removal from water supplies depend on the oxidation of manganese (+2) to the insoluble manganese (+4) of the dioxide form, with different oxidants [9]. In this respect both chlorine and hypochlorite [10], [11] could be used.



The most commonly used oxidizing agents are oxygen, potassium, permanganate, chlorine, and hypochlorites.

The costs of complying with pollution control legislation and increasing costs of raw materials, one has to seek ways to reduce their operating costs.

2. EXPERIMENTAL TECHNIQUES AND RAW MATERIALS

2.1 Materials

- Demineralized Water (DM):
Demineralized water having the composition shown in table 1 was used
- Solutions of calcium hydroxide (5g/l)
- Solutions of sodium hydroxide (100g/l)
- Solutions of sodium hypochlorite (120g/l)
- Solutions of chlorine

2.2 Equipment setup

A multistiring device having four paddles was used.

2.3 Determination of manganese concentrations in solutions and available chlorine

Manganese ions concentrations were measured using inductively coupled plasma (I.C.P.) of sequential type (atomic emission), model JY38S, having argon gas as the plasma gas [12]. It was used because of its high power of detection especially for drinking water [13] and because of its ability to work with concentrations ranging from ppb to % without dilutions and without changing the analytical conditions

2.4 Determination of available chlorine in water samples

5 ml of sample were pipetted in 250 ml conical flask, DM water was added followed by 10 ml 10% KI, 4ml HCl (1N).

Titration is performed using $\text{Na}_2\text{S}_2\text{O}_3$ (0.282 N) solution until the colour turns from brown to yellow. Titration is continued until the blue colour of the starch indicator disappears (A ml).

Free chlorine concentration is calculated from the following equation:

$$\text{Free chlorine (ppm)} = [A(\text{ml}) \times 0.01] / \text{ml of sample}$$

3. RESULTS AND DISCUSSION

3.1 Manganese removal by $\text{Ca}(\text{OH})_2$ and $\text{Na}(\text{OH})$

Fig 1 shows the effect of $\text{Ca}(\text{OH})_2$ solution dose on the % removal of manganese starting with a solution having an initial manganese Concentration of 1.47 ppm. The pH of the solution increases with the increase of $\text{Ca}(\text{OH})_2$ solution added from 7 to 10. As shown the % removal changed from 24% to 100% as the pH changed from 7 to 10. Also as the pH increases, the residual Ca^{++} concentration in the final solution increases. .

Fig 2 shows a similar experiment using a solution having an initial manganese concentration of 4.1 ppm .The pH of the solution increased from 6.6 to 10 , the percent removal reached 99% .

Fig 3 shows the use of NaOH to raise the pH of the solution for an initial Mn concentration of 4.23 ppm. An appreciable removal efficiency of 98% was achieved .

3.2 Manganese removal by aeration

Aeration was performed by pumping air, the results are shown in figures 4 and 5. As indicated, the response for manganese removal by aeration alone is not satisfactory . The removal reached 18% and 16% respectively after a period of 4 hours aeration. This might be attributed to the low solubility of oxygen in water.

3.3 Manganese removal by sodium hypochlorite

Fig 6 shows the effect of adding sodium hypochlorite solution (Concentration 1 gm free Cl_2/l) with air flow rate 2500 cm^3/min on the % removal of manganese (initial Concentration 473 ppb). As shown from the figure the % removal will depend on the Concentration of the residual Cl_2 after treatment. In all runs aeration was continued for 10 minutes.

Fig 7 also shows the same effect of hypochlorite addition on Mn removal but using chlorine concentration ten times the one before. It is clear from this figure that an appreciable increase in the efficiency of Mn removal was obtained. However, a considerable effect on pH and TDS was noticed: pH increased over 9 and TDS over 140 ppm.

Fig 8 demonstrates a third run with double concentration of the previous one. The pH increased from 8.7 to 10.2. The removal efficiency ranged from about 24% till about 57%.

Fig 9 demonstrates the effect of using higher concentration of hypochlorite solution (concentration 60 gm free Cl_2/l) on the % removal of manganese (initial concentration 767 ppb) .The removal efficiency increased to 98%, but this high efficiency was accompanied by higher value of pH of 11 and TDS of 1980 mg/l which indicates the existence of an adverse effect.

Table 2 shows a trial performed to investigate mechanical stirring and aeration , the result indicates that air is more suitable than mechanical stirring.

It is obvious that for this concentration no adverse effect on pH and TDS was detected.

From this table we conclude that increasing the radial velocity of the paddles decreases the % removal (due to bad mixing owing to vortex formation).

3.4 Effect of aeration time on the % removal using different concentrations of sodium hypochlorite solutions

Starting with water containing an initial Mn concentration of 750 ppb, different concentration of sodium hypochlorite solutions were added to show the effect of aeration time on the % removal. Fig 10 shows that as the sodium hypochlorite concentration increases, the % Mn removal increases with time.

From the figure, 20 minutes are enough to reach maximum % removal for each hypochlorite concentration. Also, there is no difference in the results obtained in cases of 300 and 400 ppm Cl_2/l solution; therefore, the optimum conditions in this case are 20 minutes aeration time and 300 ppm Cl_2/l concentration.

CONCLUSION

Using Calcium Hydroxide or Sodium Hydroxide can remove manganese from water up to 100% in case of pH 10. Aeration only may cause manganese removal up to 18%. Manganese removal by aeration (air stirring) for 10 minutes and treating the solution with sodium hypochlorite (600 ppm free chlorine/liter resulted in removal percentage up to 97%, it was observed that this process resulted in an increase in the pH value up to 11 and TDS up to 1980 ppm. It was noticed that the removal percentage depends on the following conditions:

- a. Sodium hypchlorite concentration
- b. Aeration time

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Element	Amount
Mg	3.28 ppb
Ca	4.11 ppb
Cd	Not Detected
Ni	Not Detected
Fe	20.50 ppb
Zn	<10.00 ppb
Mn	<10.00 ppb
Cr	Not Detected
Co	Not Detected
1u	<5.00 ppb
Pb	Not Detected

Table (1): I. C. P. Analysis Report of DM Water

Chlorine Concentration (ppm)	Aeration time (min)	No. of revolutions (rpm)	Mn Concentration (ppb)	TDS (mg/l)	% Removal	pH
-	-	-	750	11.5	-	6.84
1	10	-	615	35.5	18	7.49
1	-	10	633	36	15.6	7.43
1	-	100	728	36	2.93	7.43

*Table (2): Comparison Between Stirring By Air And Paddles
Using 1 ppm Chlorine Concentration*

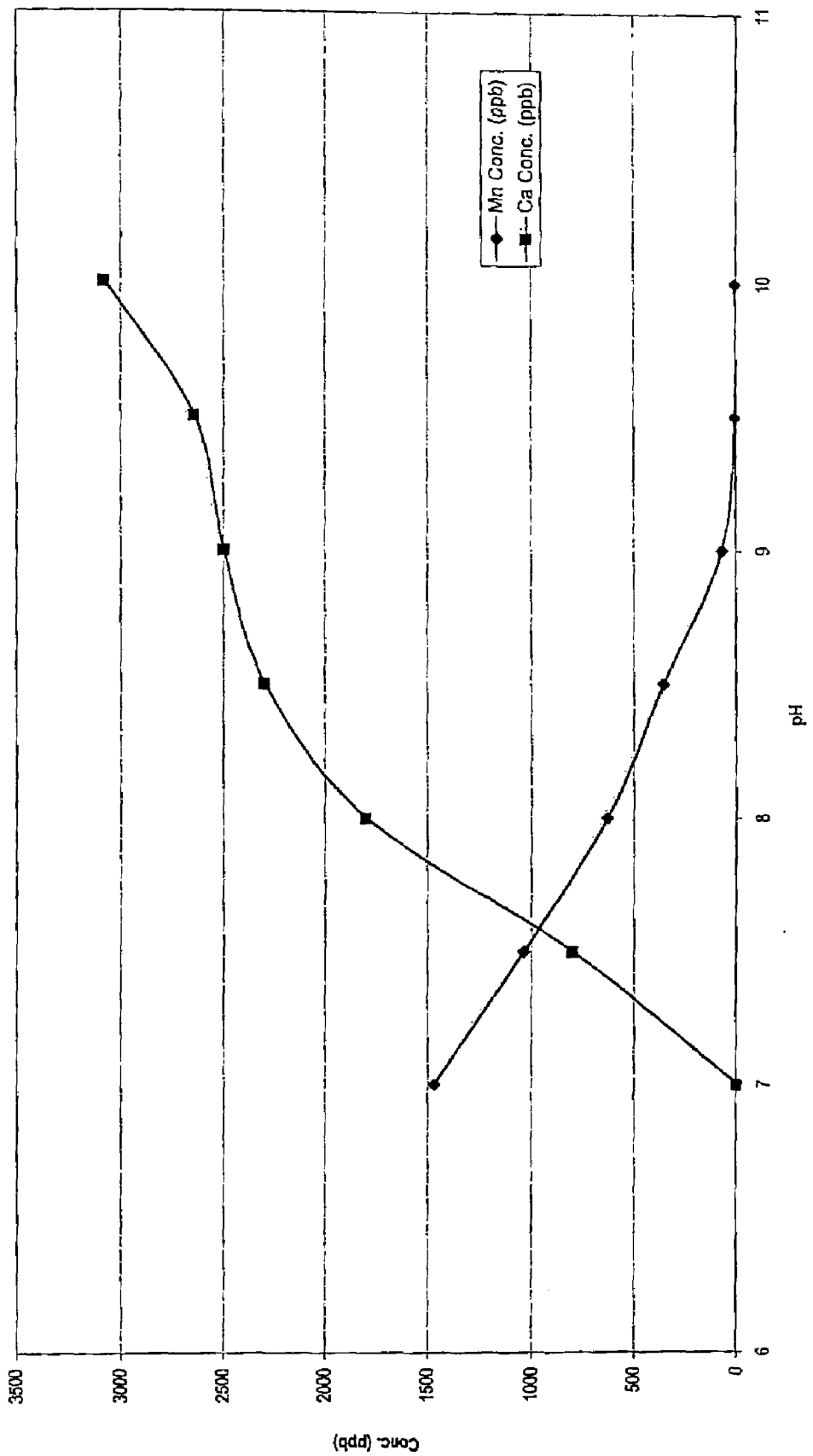


Fig. 1 Effect of $\text{Ca}(\text{OH})_2$ on the Manganese Concentration

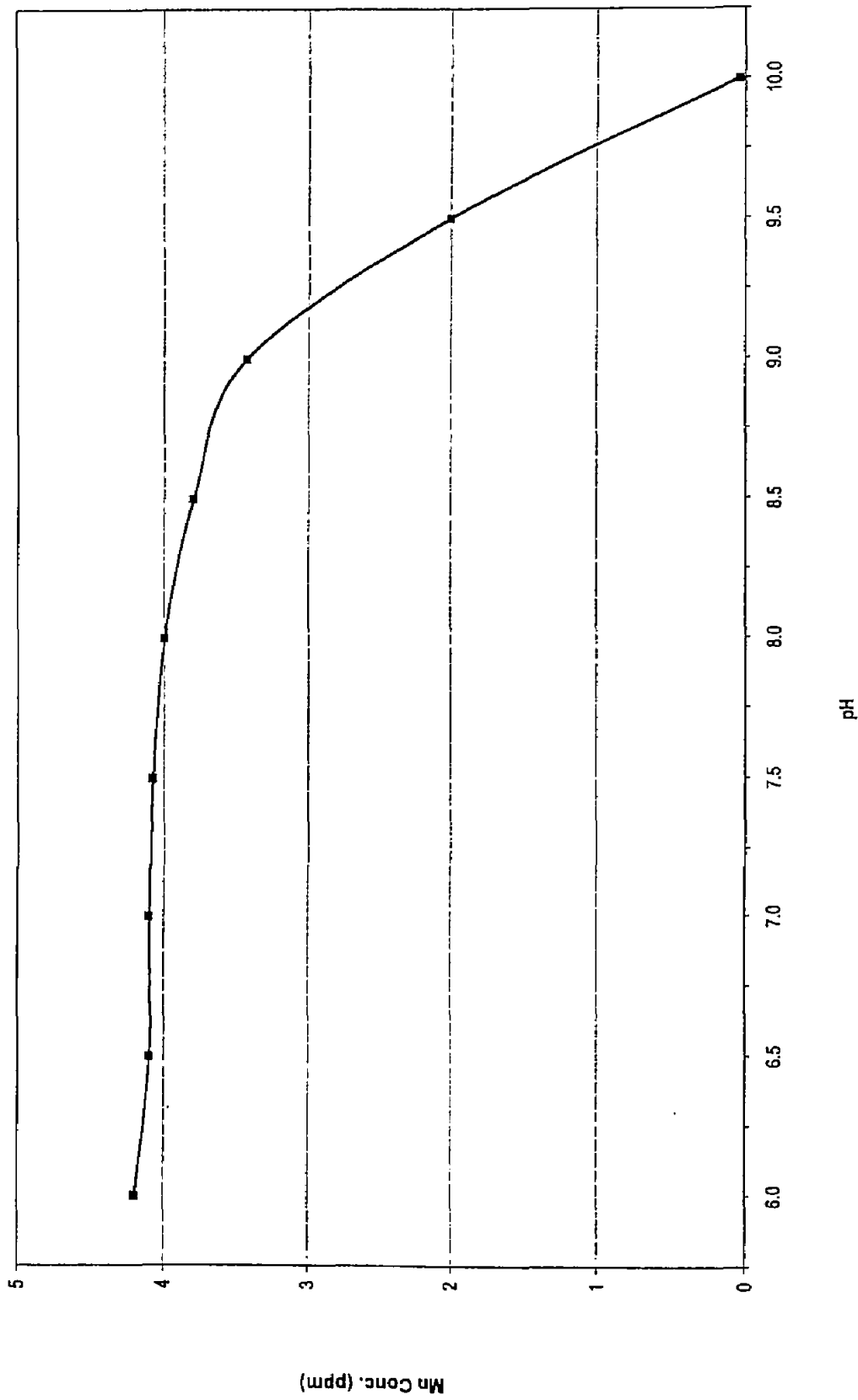


Fig. 2 Effect of Ca(OH)_2 on the Manganese Concentration (for an Initial Mn Concentration 4 ppm)

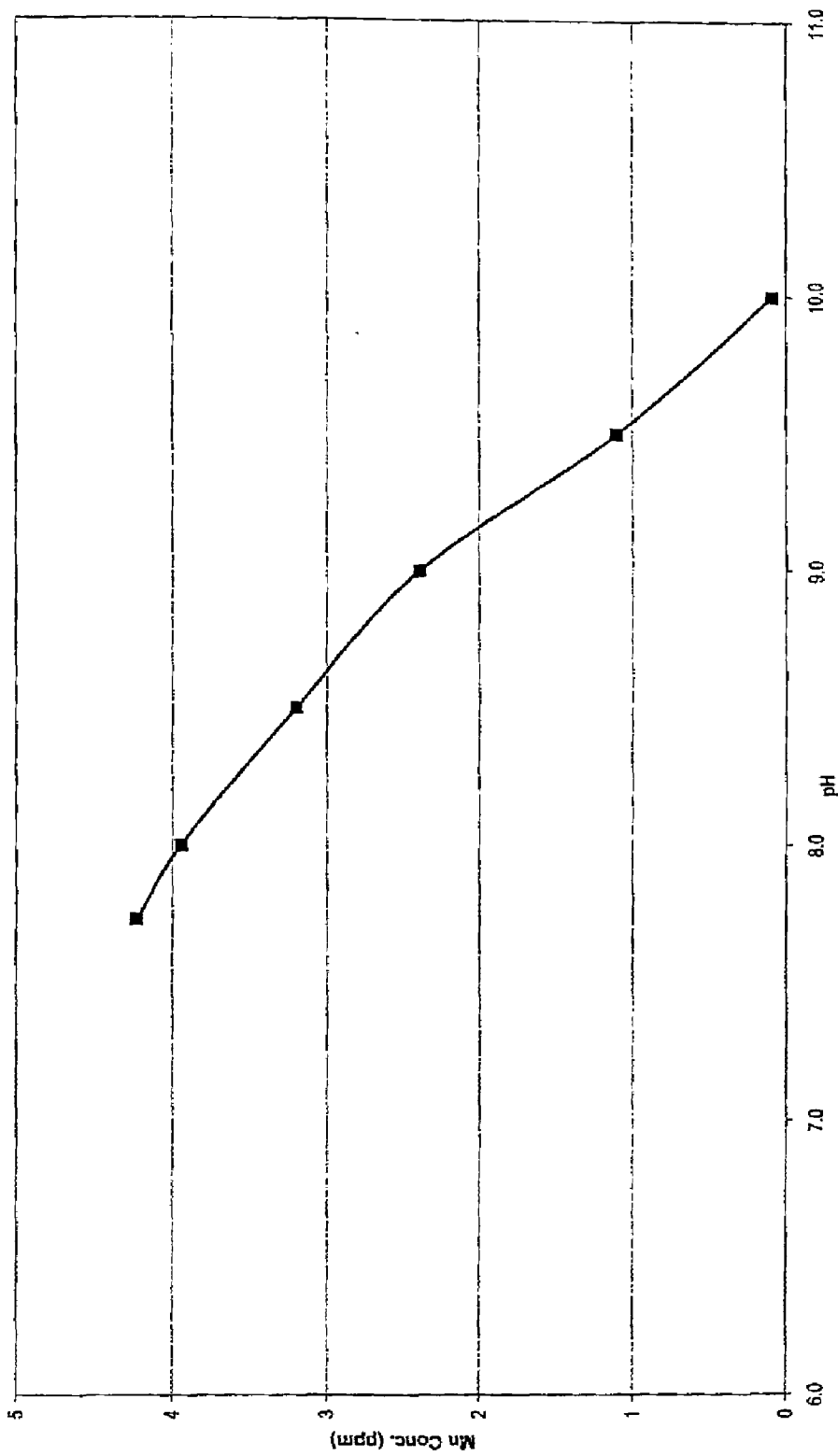


Fig. 3 Effect of NaOH on the Manganese Concentration

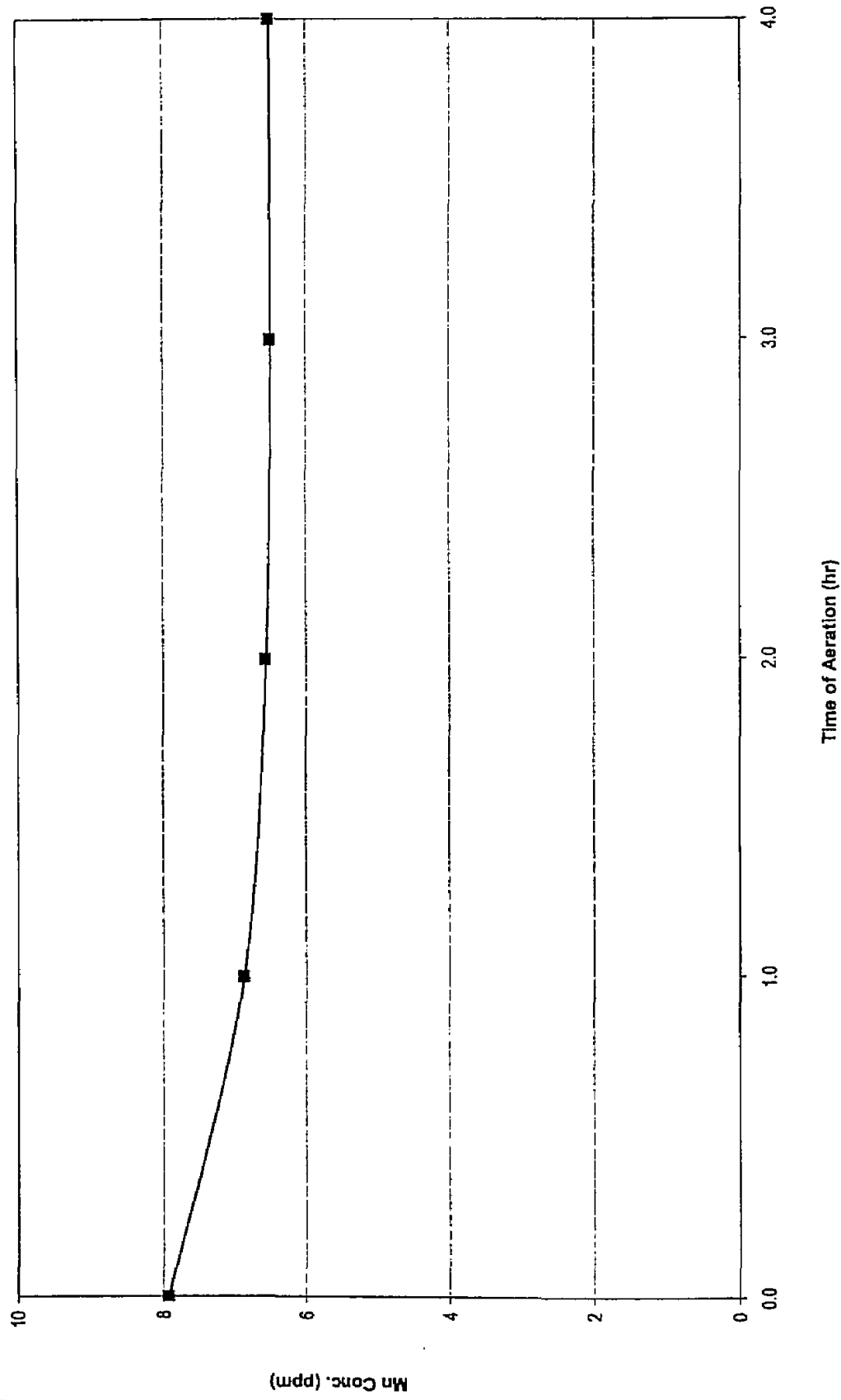


Fig. 4 Effect of Air on Manganese Removal (for an Initial Mn Concentration 7.93 ppm & Air flowrate 2500 cm³/min)

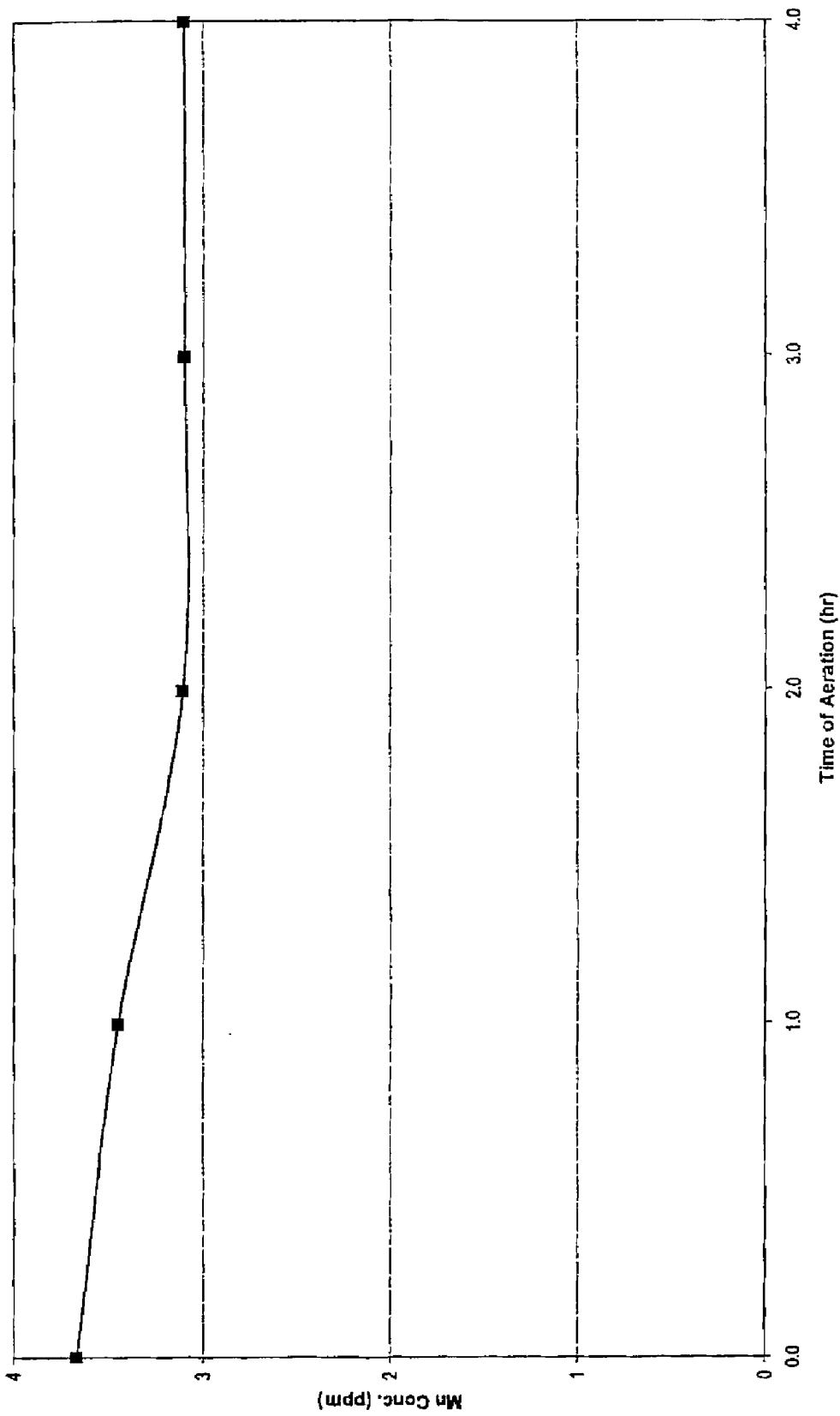


Fig.5 Effect of Air on Manganese Concentration (for an Initial Mn Concentration 3.67 ppm & Air flowrate 2500 cm³/min)

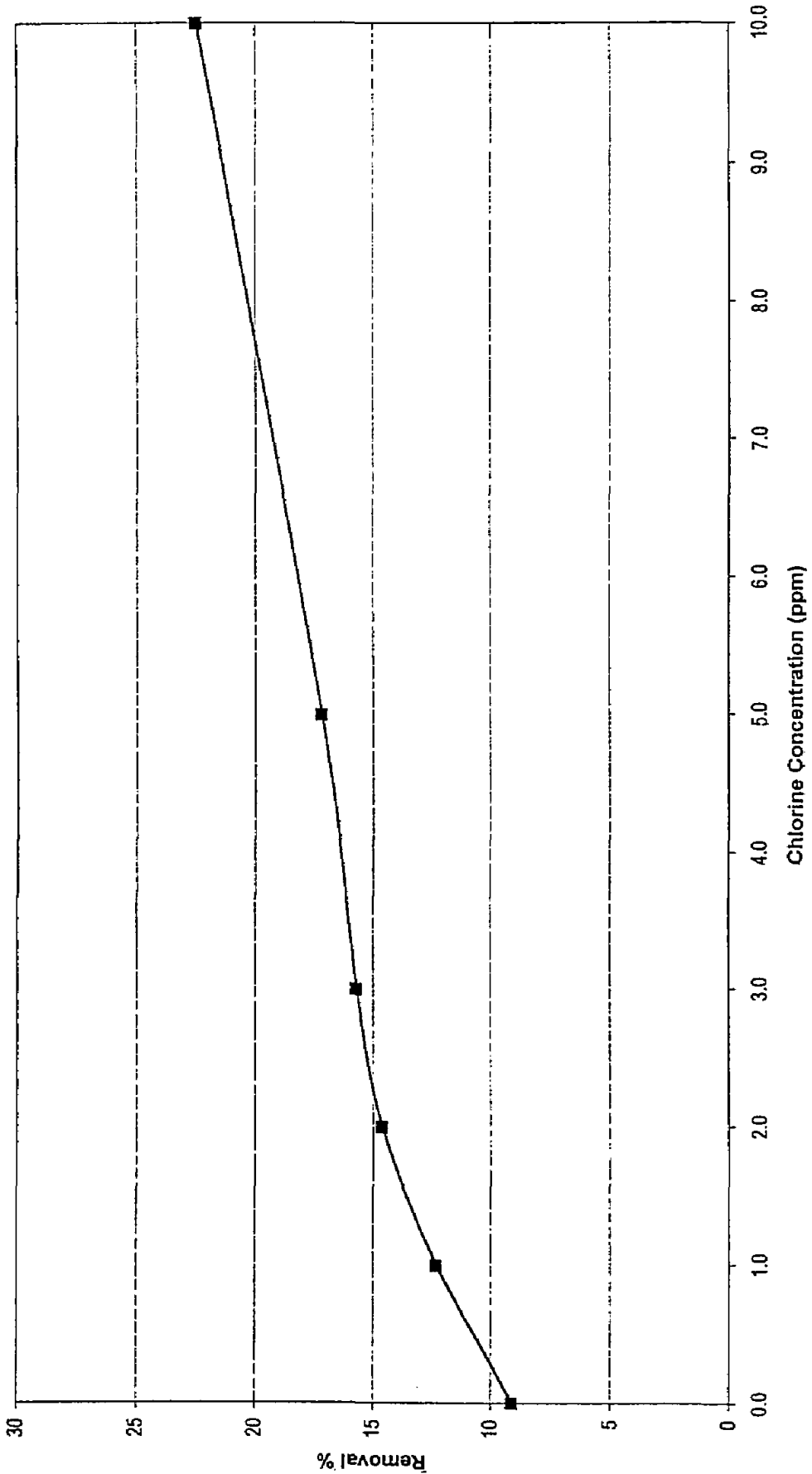


Fig. 6 Effect of Sodium Hypochlorite Concentration (1 gm free Cl₂/l) on Manganese Removal (Air Flowrate 2500 cm³/min)

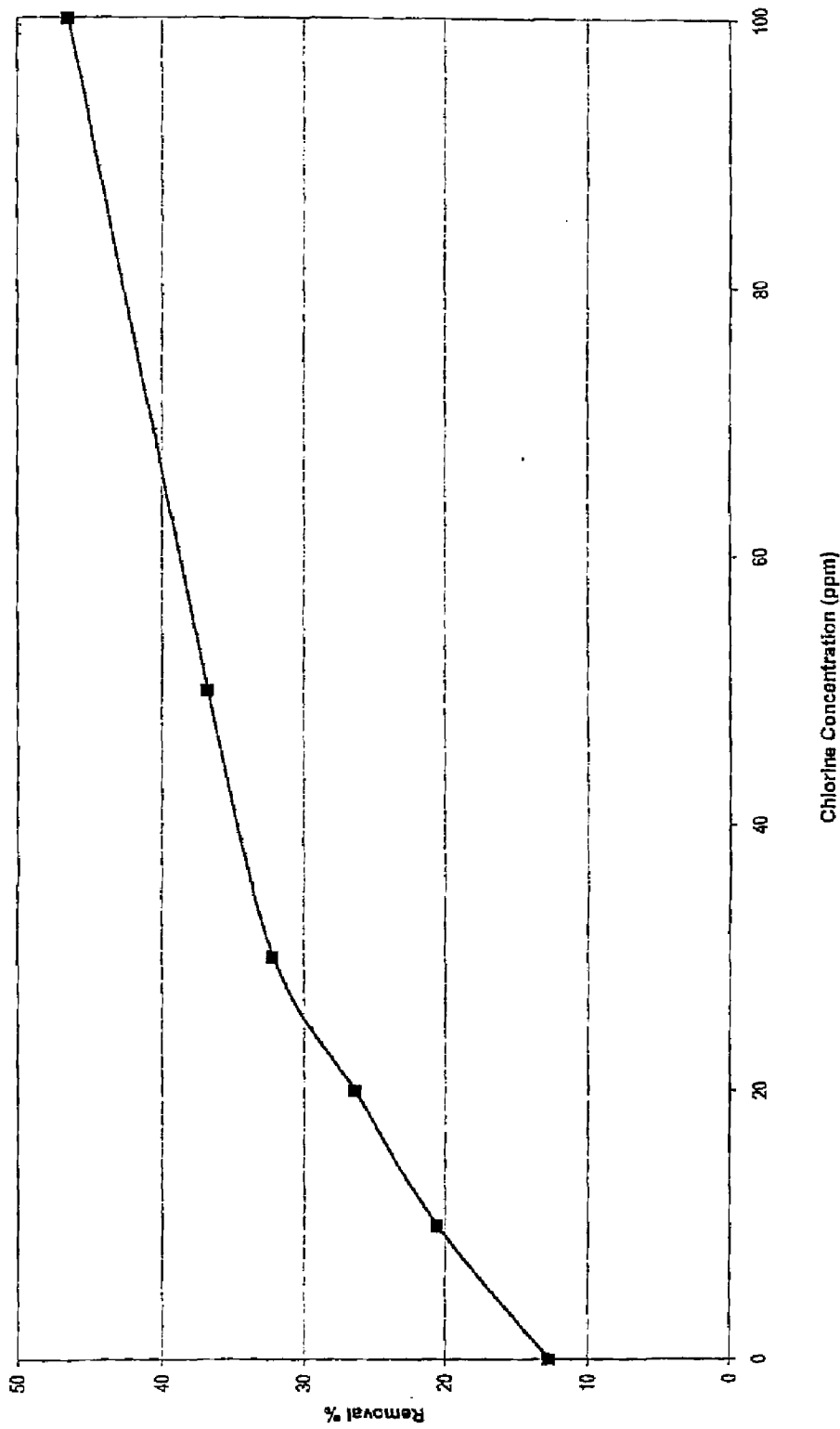


Fig. 7 Effect of Sodium Hypochlorite Concentration (10 gm free Cl₂/l) on Manganese Removal (Air Flowrate 2500 cm³/min)

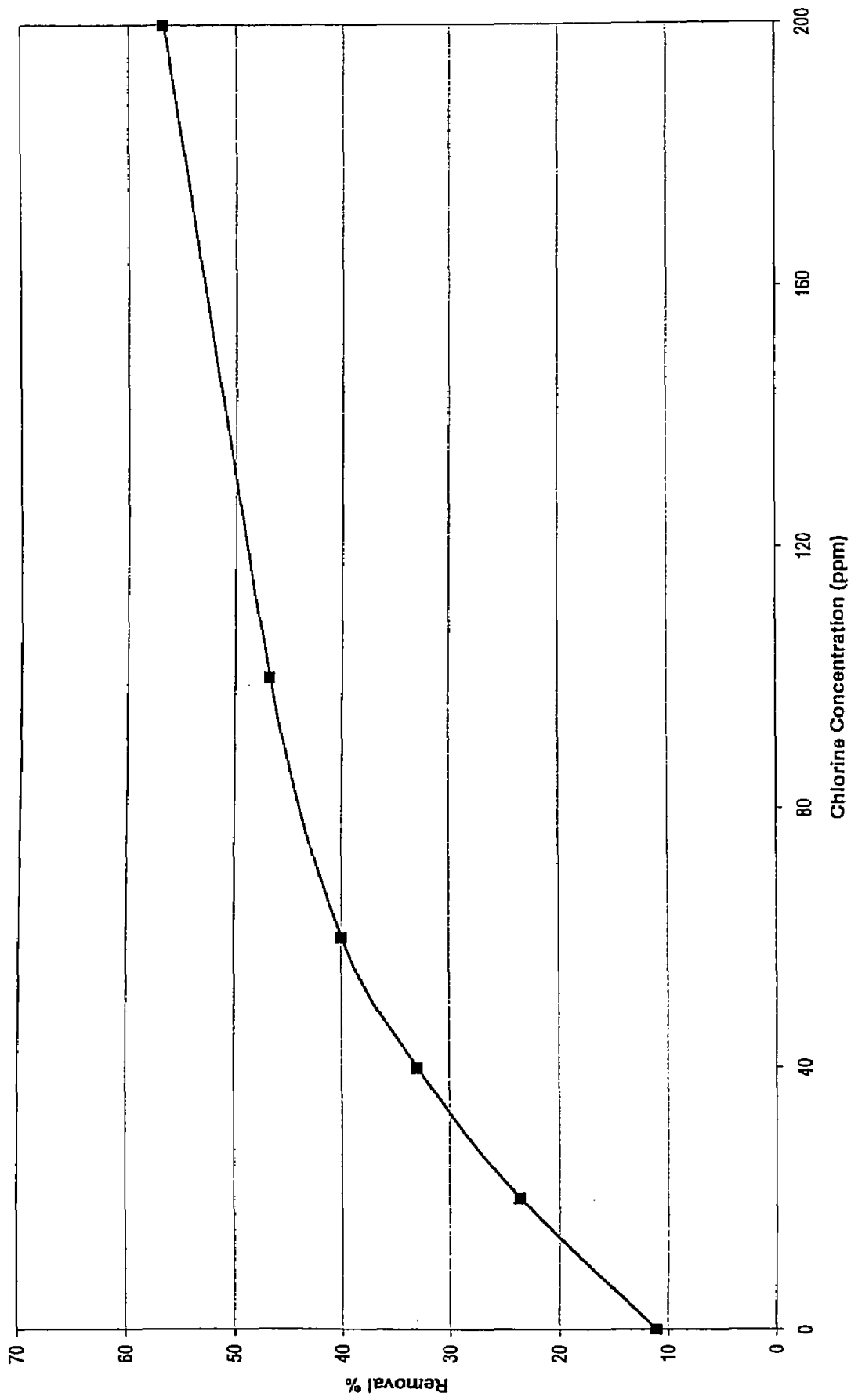


Fig. 8 Effect of Sodium Hypochlorite Concentration (20 gm free Cl_2/l) on Manganese Removal (Air Flowrate 2500 cm^3/min)

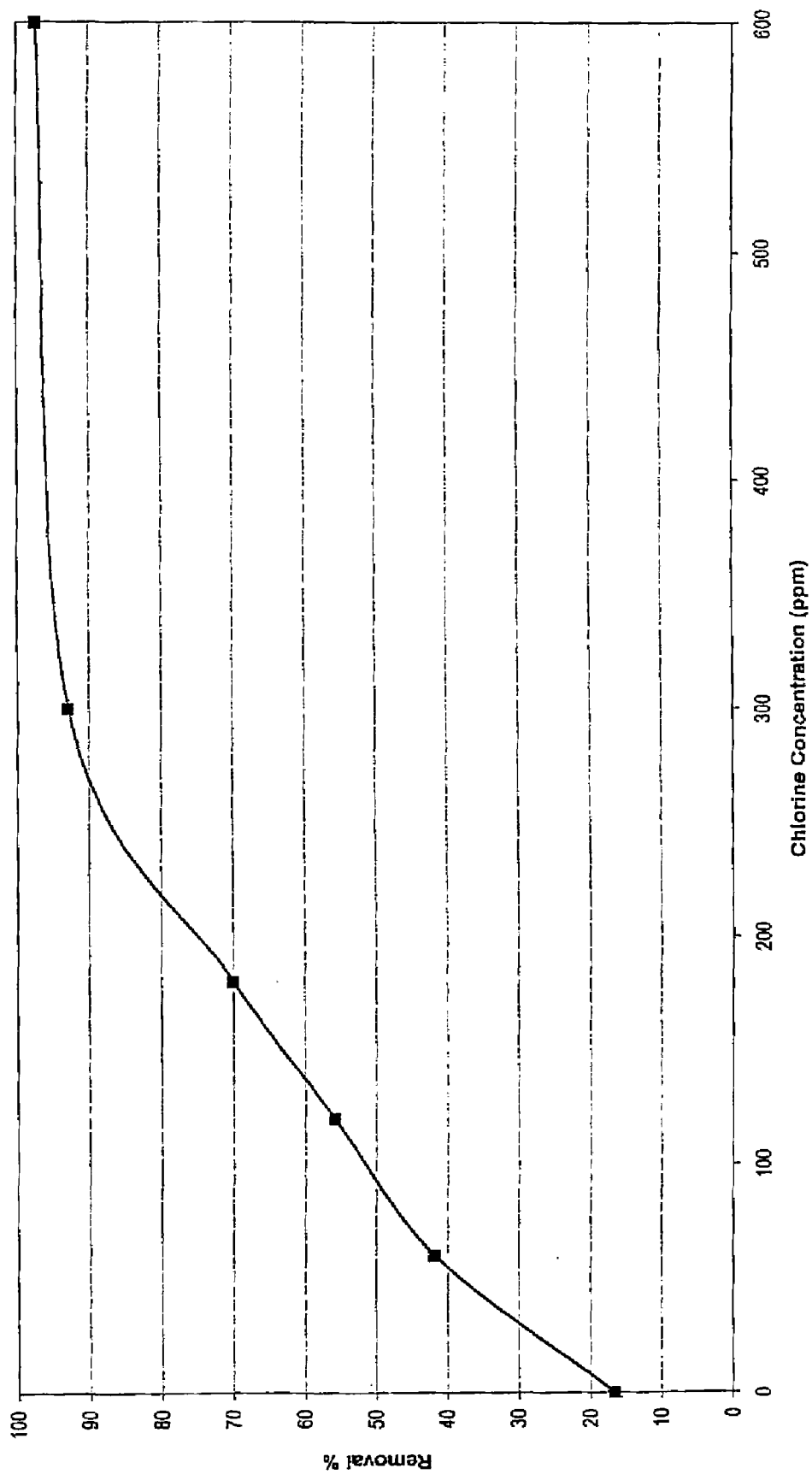


Fig. 9 Effect of Sodium Hypochlorite Concentration (60 gm free Cl_2/l) on Manganese Removal (Air Flowrate $2500\text{ cm}^3/\text{min}$)

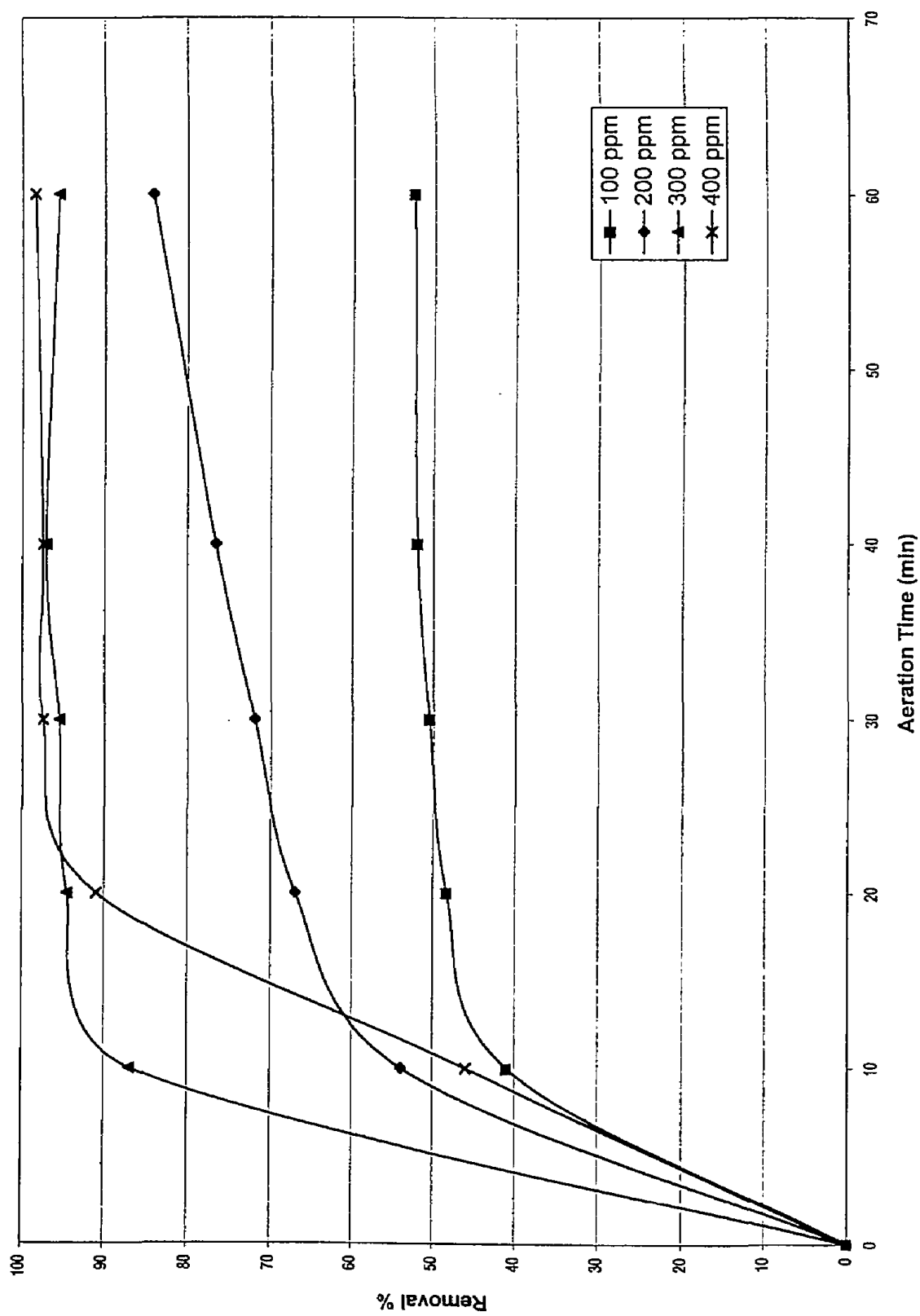


Fig. 10 Effect of Sodium Hypochlorite Concentration (100, 200, 300 & 400 ppm free Cl₂/l) on Manganese Removal at Different Aeration Time