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CONCLUSIONS

- 1- The mathematical model adequately describe the influences of studied variables through out the studied ranges of these variables.
- 2- The high flow rate leads to minimize residence time inside the resin bed. This means higher flow rate gives shorter breakthrough time.
- 3- It was shown that the longer bed depth gives sufficient contact time of each particle with hard water. This means longer breakthrough time.
- 4- Higher influent hardness concentration in the solution leads to higher mass transfer rate through the Nernst film until it exceeds the diffusion rate through the resin beads and consequently the system exhibits particle controlled kinetics that means deeper reaction zone. This condition leads to shorter breakthrough time.
- 5- It was found that the leakage of hardness increases with increasing hardness concentration of the influent solution.

NOMENCLATURE

| | |
|----------------|---|
| N | Number of Experiments |
| P | Number of Variables |
| TEF | Tetrafluoroethylene |
| X ₁ | Flow Rate of hard Water |
| X ₂ | Bed Depth of Cation Exchanger |
| X ₃ | Hardness Concentration |
| Y | Observed Value of Response (dependent variable) for Experiments |

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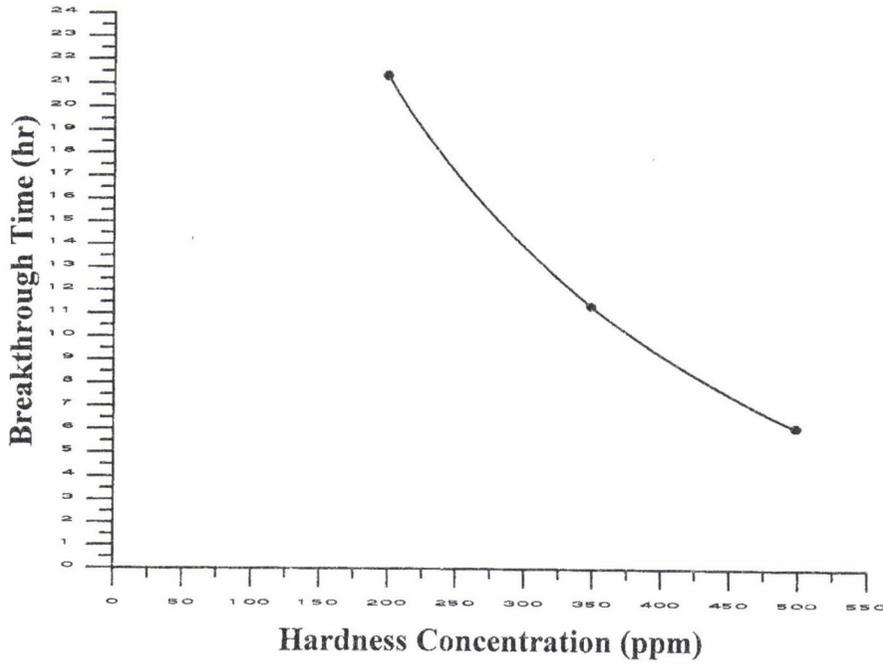


Fig. (6) Effect of Different Hardness Concentration on Breakthrough Time at Flow Rate = 3.04 L/hr and Bed Depth = 0.3 m.

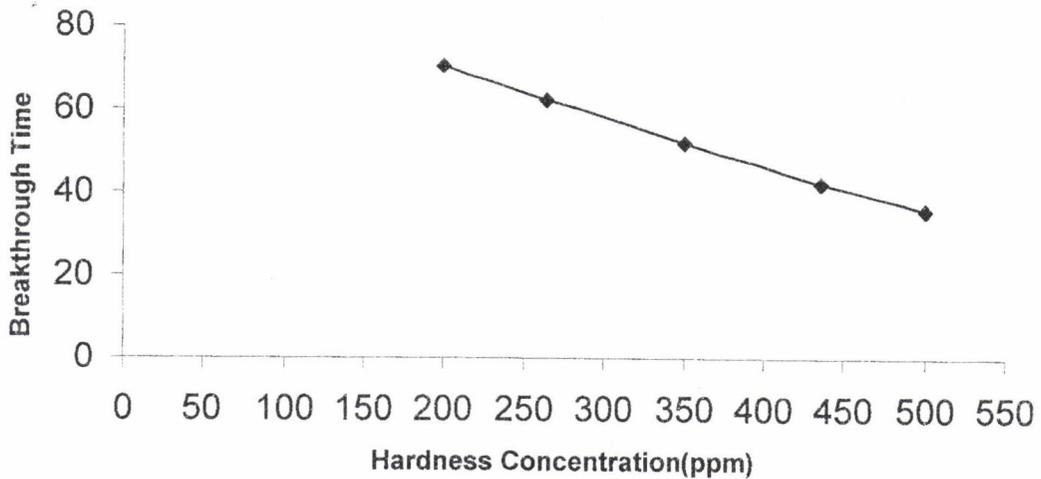


Fig. (7) Effect of Different Hardness Concentration on Breakthrough Time at Optimum Flow Rate = 1.013 L/hr and Optimum Bed Depth = 0.5 m.

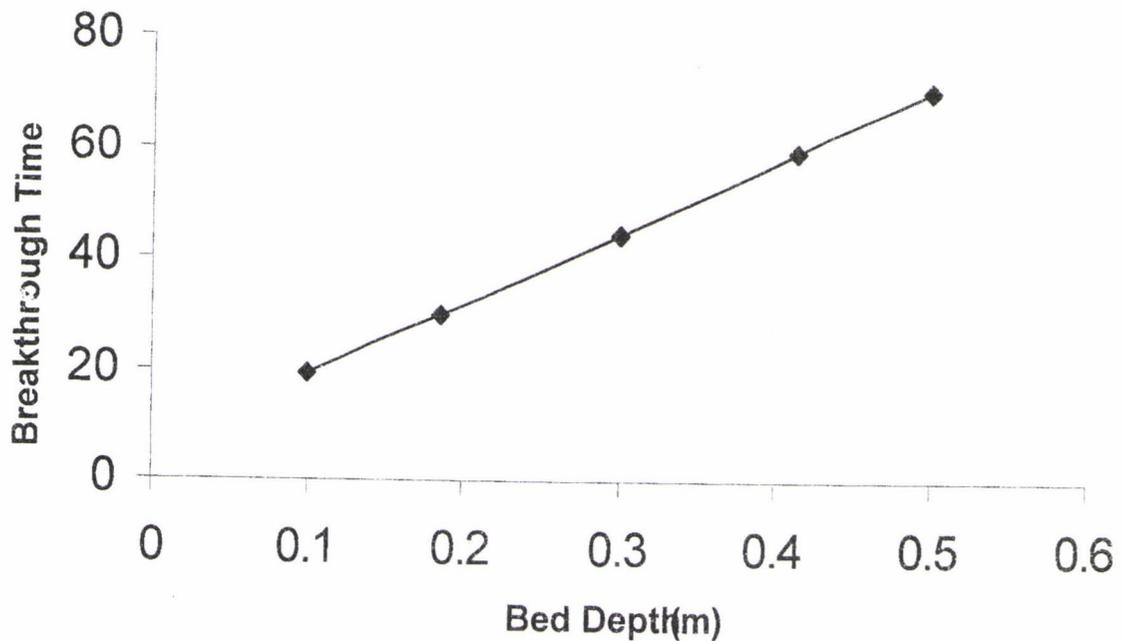


Fig. (5) Effect of Different Bed Depth on Breakthrough Time at
Optimum Flow Rate = 1.013 L/hr and Optimum Hardness
Concentration = 200 ppm

- 3- Effect of Hardness Concentration: The breakthrough time was plotted against different hardness concentrations (200, 350, and 500 ppm) at constant flow rate (3.04 L/hr), and bed depth (0.3 m) in Fig. (6). This figure shows that the breakthrough time decreased with the increasing of the hardness concentration. This is because when concentration of the influent solution increases, the leakage increases, this is in good agreement with Prajapati *et al.* [1985]. This leakage it leads to earlier breakthrough point, because the exchange capacity will decrease, and this causes shorter service cycle. This phenomena is in good agreement with Keller [2001], and Kunin [1963]. Fig. (7) demonstrated the relationship between breakthrough time and hardness concentration by using Eq.(4). In this figure the breakthrough time was plotted against different hardness concentration (200, 263.39, 350, 436.5, and 500 ppm), optimum flow rate is (1.013 L/hr), and optimum bed depth is (0.5 m).

2- Effect of Bed depth: Three experiments were carried out at different bed depths (0.1, 0.3, and 0.5 m) with constant flow rate (3.04 L/hr), and hardness concentration (350 ppm). **Fig. (4)** shows that the breakthrough time increases with increasing bed depth. This can be explained as follows: Longer bed depth gives longer reaction zone “which is the region of the resin bed that the reaction occurs between the ions in the solution and those in the resin”. When the reaction zone increases, additional spaces will be available for hardness ions to be exchanged with the Na^+ ions in the resin, and consequently later, the breakthrough time will increase. **Fig. (5)** illustrates the effect of bed depth on breakthrough time by using Eq.(4) at different bed depth (0.1, 0.185, 0.3, 0.415, and 0.5 m), optimum flow rate is (1.0134 L/hr) and optimum hardness concentration (200 ppm). Because of this relation, longer bed depth is recommended when high quality effluent is desired.

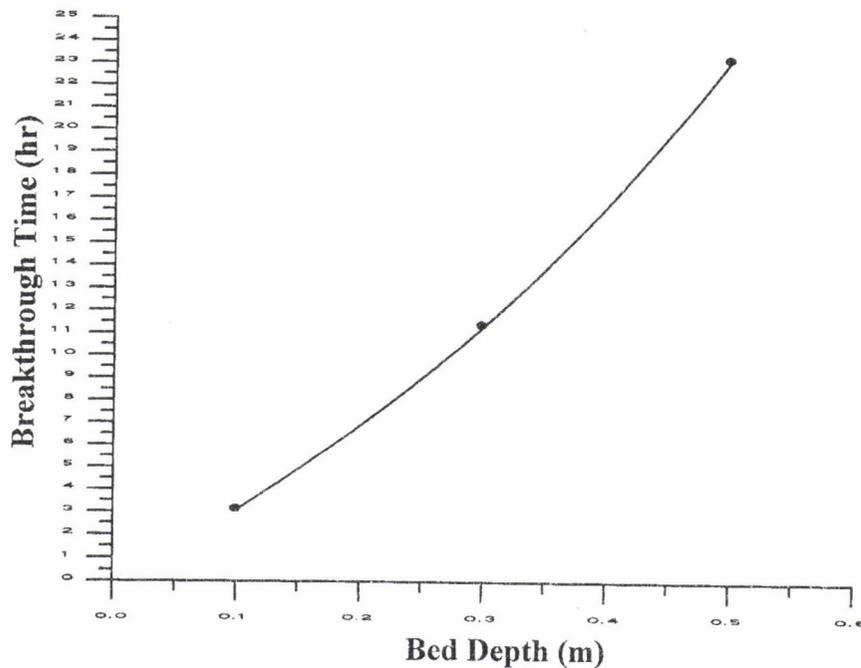


Fig. (4) Effect of Different Bed Depth on Breakthrough Time at Flow Rate = 3.04 L/hr and Hardness Concentration = 350 ppm

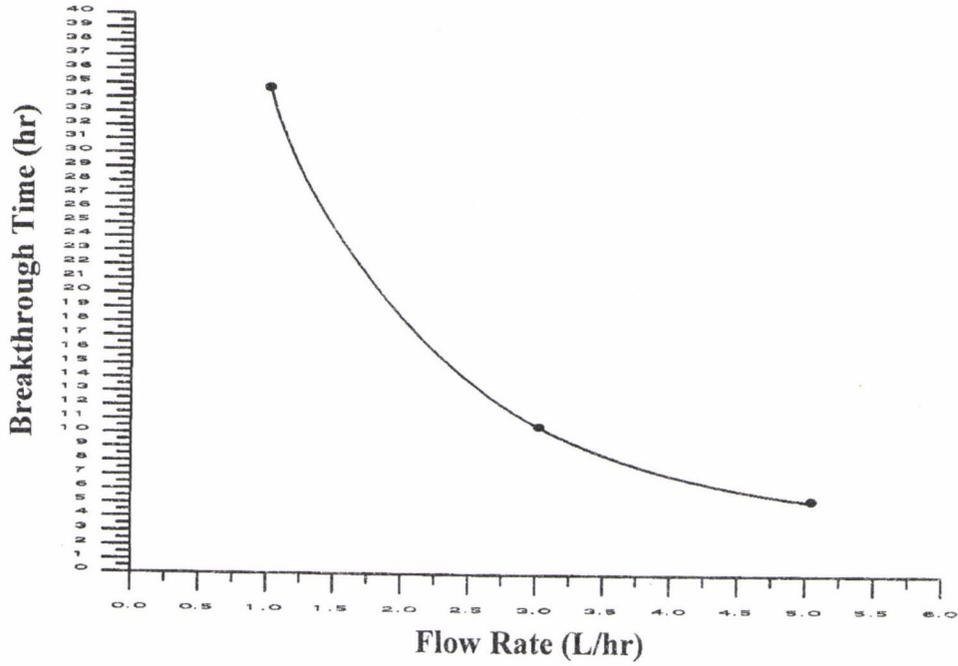


Fig. (2) Effect of Different Flow Rate on Breakthrough Time at Bed Depth = 0.3 m, and Hardness Concentration = 350 ppm

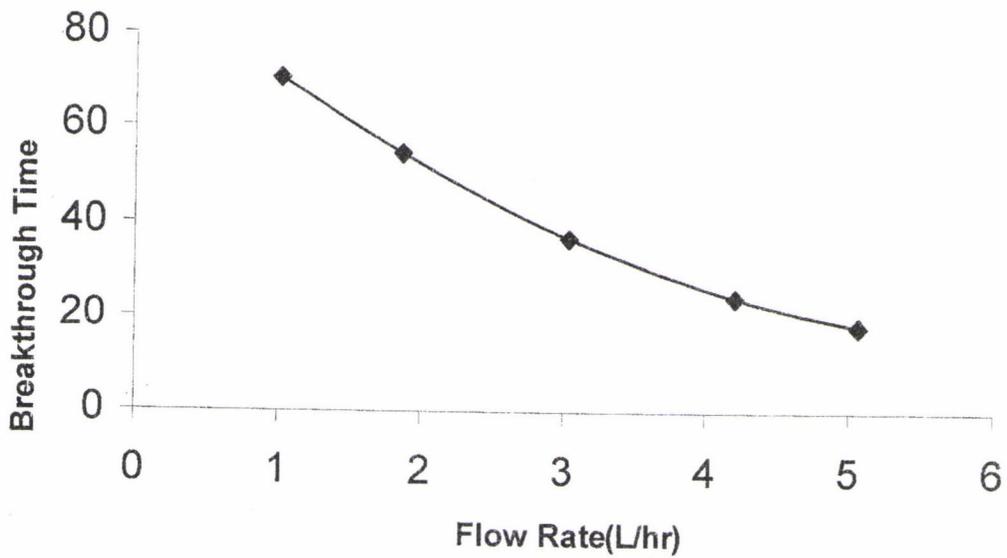


Fig. (3) Effect of Different Flow Rate on Breakthrough Time at Optimum Bed depth = 0.5 m and Optimum Hardness Concentration = 200ppm By using Eq. (4)

RESULTS AND DISCUSSION

Estimation: The Coefficients Of The Proposed Method

The coefficients of the proposed second order polynomials are represented in the following models:

$$Y_{\text{Breakthrough time}} = 1.56 - 0.106 x_1 + 0.234x_2 - 0.114x_3 - 0.01x_1x_2 + 0.022x_1x_3 \\ + 0.03x_2x_3 - 0.077x_1^2 - 0.004x_2^2 + 0.000063x_3^2$$

Optimum operating conditions at maximum breakthrough time were determined by implementing pattern move Hooks and Jeeves optimization technique.

Flow rate = 1.0134 L/hr

Bed depth = 0.5 m

Hardness concentration = 200 ppm.

These three variables have different effect on breakthrough time as follows:

- 1- Effect of Flow rate: **Fig. (2)** illustrates the effect of different flow rates (1.013, 3.04, and 5.06L/hr) on the breakthrough time of the cation exchanger with constant other conditions, bed depth (0.3m) and hardness concentration (350 ppm). This figure shows that the breakthrough time decreases with increasing flow rates. This relation can be explained as follows: A lower flow rate will cause longer service cycle. This flow rate gives sufficient contact time for the hardness ions to be exchanged with sodium ions in the resin particles. Because of low flow rates, equilibrium was established as the solution reached a new layer of the resin. A higher flow rate can exceed the kinetics of the resin. This means that the resin cannot exchange ions fast enough. Exhaustion band forms that contain both regenerated and exhausted resin. As the flow rate increases this band will expand. This expansion reduces the amount of usable resin in the unit. Therefore, when higher flow rates are used, it is important to know that the hardness leakage will increase. This phenomena is in a good agreement with Keller [2002] and Blaxall [Purolite, 1995]. The hardness leakage is the amount of the hardness ions that are being removed from the solution, and appears in the column effluent during the course of the service cycle. **Fig. (3)** shows the relation between flow rate and breakthrough time by using Eq.(4), at different flow rates (1.013, 1.87, 3.04, 4.21, and 5,067 L/hr), optimum bed depth is (0.5 m) and optimum hardness concentration (200 ppm).

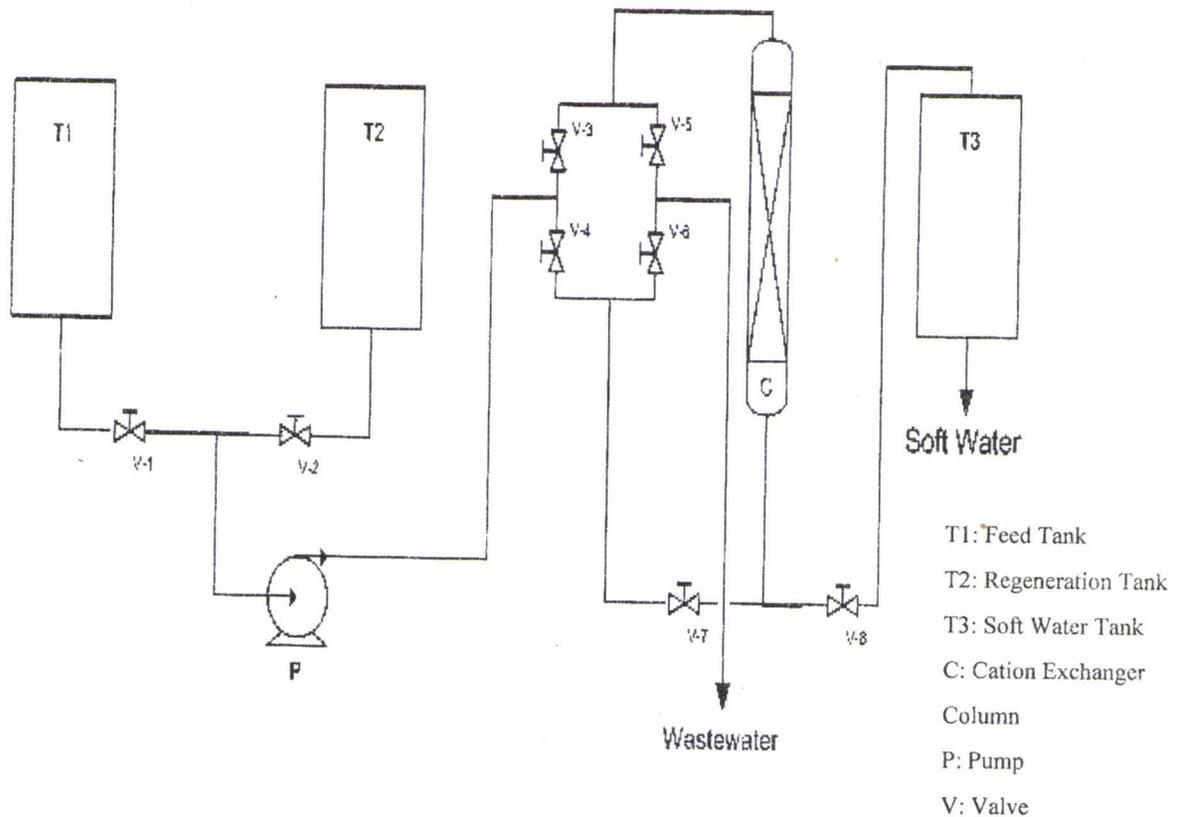


Fig. (1) Schematic Diagram of Softening Pilot Plant

EXPERIMENTAL PROCEDURE

Backwashing: The cation exchanger in column C was washed in an upwards direction (counter - current) with flow rate 8 - bed volume/hr for 10 to 15 minutes using hard water to remove any particulate matter, to clear the bed of any air pockets or bubbles, and to reclassify the resin particles as much as possible so as to active minimum resistance to flow in subsequent operation. During upflow backwash, the resin bed should be expanded in volume by 50 - 80% pumped water for backwashing.

Regeneration: Regeneration of the cation exchanger was carried out using 10% NaCl solution. The solution flowed down from tank T2 into column C (co - current) with a flow rate of 4 - bed volume /hr for 30 - minutes.

Rinse Process:

Slow Rinse: Hard water was pumped from tank T1 downward (co - current) into column C by the dosing pump P with a flow rate of 4 - bed volume /hr. Each slow rising step lasted 20 minutes.

Quick Rinse: Hard water was pumped from tank T1 downward (co - current) into column C by the dosing pump P downwards with a flow rate of 20 - bed volume /hr. Each quick rinsing lasted 30 minutes.

Service or Loading Cycle: Hard water was pumped using dosing pump P from tank T1 into column C (cation exchanger) with a flow rate of 20 - bed volume /hr. The flowing solution was kept during the experiment with continuous monitoring of the hardness of effluent stream until break point of hardness 4 ppm was detected.



MATERIALS

- 1- Ion exchange resin: Softening by exchange of calcium and magnesium by sodium is the major industrial application of ion exchange. The suitable type of ion exchanger for use with hardness water is strongly acidic cation exchanger, the name matrix structure is Amberlite IR - 120 Styrene DVB gel. The specifications of this resin are listed in **Table (2)**.

Table (2) Physical Properties of Strongly Acidic Cation Exchangers IR-120

| | |
|-------------------------|--|
| Appearance | Reddish - brown |
| Form | Spheres |
| Matrix | Styrene - Divinylbenzene copolymer |
| Functional groups | -SO ₃ ⁻ |
| Ionic form | Na ⁺ |
| Specific gravity | 1.28 (Na ⁺ form) |
| Net weight as shipped | 53 lb/cu ft (0.68 Kg/m ³) |
| Moisture content | 44 - 52% |
| Particle size | 0.5 mm |
| Total exchange capacity | 1.9 - 2.15 meq/ml |
| Chemical stability | Unaffected by non- oxidizing acids and bases and by common solvents. |

- 2- Regeneration Solution: The strongly acidic cation exchangers were regenerated with 10% sodium chloride solution.
- 3- Feed water: For the laboratory experimental work, tap water mixed with either calcium chloride to increase its hardness or with deionized water to decrease its hardness. The hardness of ordinary tap water is around 300 ppm and so the procedure of increasing or decreasing the water hardness depends on simple calculations (Reem A. Al - Rawi, M Sc thesis, 2002).
- 4- EDTA: Ethylene diamine tetraacetic acid disodium salt is used as titrating agent.

EQUIPMENTS FOR EXPERIMENTAL WORK

A schematic representation of the experimental equipments are shown in **Fig. (1)**.

A glass Q.V.F column was used (2.54 cm internal diameter) and (100 cm long).

Three plastic containers were used. The first one as feed container, the second one as regenerant container and the third one as a receiver for soft water, capacity of each one of them is 25 liters.

Eight poly tetra fluoro Ethylene (Teflon) valves were used to control opening and closing.

The regeneration solution and feed solution were pumped from their containers through the resin bed by dosing pump (Prominent Electronic, type E 0407 Gmbh sweden) of 0 - 6.3 liter/hr capacity.

Table (1) The Coded and Real Values of the Experiment Conducted According to Box - Wilson Method

| Run No. | Coded Variables | | | Real Variables | | |
|---------|-----------------------------|-----------------------------|------------------------------|------------------|---------------|-------------------|
| | X ₁ Flow rate | X ₂ Bed depth | X ₃ Hard. Conc | Flow rate (L/hr) | Bed depth (m) | Hard.Co nc. (ppm) |
| 1 | +1 | +1 | +1 | 4.21 | 0.415 | 436.5 |
| 2 | -1 | +1 | +1 | 1.87 | 0.415 | 436.5 |
| 3 | +1 | -1 | +1 | 4.21 | 0.185 | 436.5 |
| 4 | -1 | -1 | +1 | 1.87 | 0.185 | 436.5 |
| 5 | +1 | +1 | -1 | 4.21 | 0.415 | 263.39 |
| 6 | -1 | +1 | -1 | 1.87 | 0.415 | 263.39 |
| 7 | +1 | -1 | -1 | 4.21 | 0.185 | 263.39 |
| 8 | -1 | -1 | -1 | 1.87 | 0.185 | 263.39 |
| 9 | 1.732 | 0 | 0 | 5.067 | 0.30 | 350 |
| 10 | 0 | 1.732 | 0 | 3.04 | 0.50 | 350 |
| 11 | 0 | 0 | 1.732 | 3.04 | 0.30 | 500 |
| 12 | -1.732 | 0 | 0 | 1.013 | 0.30 | 350 |
| 13 | 0 | -1.732 | 0 | 3.04 | 0.10 | 350 |
| 14 | 0 | 0 | -1.732 | 3.04 | 0.30 | 200 |
| 15 | 0 | 0 | 0 | 3.04 | 0.30 | 350 |
| 16 | 0 | 0 | 0 | 3.04 | 0.30 | 350 |
| 17 | 0 | 0 | 0 | 3.04 | 0.30 | 350 |
| 18 | 0 | 0 | 0 | 3.04 | 0.30 | 350 |

Every 15 minutes (10 ml) sample was taken out periodically from the outlet of the column for analysis until break point that already was reached which is equal to (4 ppm) hardness concentration.

The experiments are conducted in the following sequence:

- 1- Removing the hardness from water by ion exchangers.
- 2- Measuring the breakthrough time when effluent concentration equal to (4 ppm).
- 3- Find suitable relationship between the three independent variables (flow rate, bed depth, and hardness concentration) and breakthrough time.

EXPERIMENTAL DESIGN

An experimental design for fitting a second order model must have at least three levels for each factor so that the model parameters can be estimated (i.e. variables are usually called factors and the particular value of the variable is called the level). The most widely used design for fitting a second order model is the Box - Wilson rotatable central composite design. The design principle includes three types of combinations, the axial, factorial, and center points. Axial points include each factor at its extreme levels with the other factors at their center - point level. The center point is a single test at the average level of each factor. For purposes of estimating experimental error, the center point is usually repeated three to five times during the experiment. Designs for any number of factors can be developed from these principles. The value for rotatability depends on the number of variables P (i.e., for $P = 2$; $\alpha = \sqrt{P} = 1.414$ and for $P = 3$; $\alpha = \sqrt{P} = 1.732$).

A preliminary step is to setup the relationships between the coded levels and the corresponding real variables. These relationships are as follows:-

$$X_{\text{coded}} = \frac{\left[\frac{X_{\text{actual}} - X_{\text{center}}}{X_{\text{center}} - X_{\text{min}}} \right]}{\sqrt{P}} \quad \text{Eq.(2)}$$

The number of experiments N needed is estimated according to the following equation:

$$N = 2^P + 2P + 1 \quad \text{Eq.(3)}$$

EXPERIMENTAL WORK

Operating Conditions

In order to design the experiments, the operating conditions of the variables are the first specified, thus:

X_1 = Flow rate of hard water 20 BV (1.013 to 5.067 L/hr)

X_2 = Bed depth of cation resin from 0.1 to 0.5 m (using column with 2.5 cm in diameter)

X_3 = Hardness concentration from 200 - 500 ppm

According to Eq. (3) the total number of experiments (N) is:-

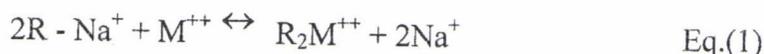
$$N = 2^3 + 2(3) + 1 = 15$$

Where 2^3 represent the factorial points, the $2(3)$ are the axial points, and 1 center point.

According to the experimental design of the three variables there are 15 experiments plus 3 at the center point to estimate the experimental error. These experiments carried out in a sequence shown in **Table (1)**, where the coded values + 1.732, - 1.732, and 0 represent the maximum, minimum, and average values respectively.

Softening of water involves beads form conventional gel polystyrene sulphonate cation exchange resins designed for use in industrial or household water conditioning equipment. It removes the hardness ions, e.g. calcium and magnesium, replacing them with sodium ions. When the resin bed is exhausted and hardness ions being to breakthrough, capacity is restored by regeneration with common salt. The capacity obtained depends largely on the amount of salt used in the regeneration [Purolite 2G00; AWWA, 1971]

The reaction can be represented by the following equation.



Where R is resin matrix and M^{++} is magnesium or calcium ions.

Ion exchange is a chemical treatment process used to remove unwanted ionic species from wastewater. It is basically a simple process based on reversible interchange of ions between liquid and solid (that is, the resin) with no permanent changes in the structure of the solid [ABB, 1999; Kirk-Othmer, 1981].

The ions are not destroyed but rather are removed from the waste stream and concentrated on the resin, where they can be more easily handled [Bolto and Pawlowski, 1987]. Cation exchange resins (used in softeners) contain fixed electronegative charges, which interact with mobile counter ions having the opposite or positive charge.

The rate of ion exchange depends, upon rates of the following individual processes: (1) movement of ions from bulk solution to the external surface of an exchanger particle; (2) diffusion of the ions through the pores; (3) ions exchange; (4) diffusion of the exchanged ions outward to the surface of the solid; (5) movement of exchanged ions into bulk of solution [Ions Exchange, 1998; Treybal, 1981].

There are four primary types of ion exchangers:-

- 1- Strongly cation exchange resins, containing sulfonic acid groups or the corresponding salts.
- 2- Weak cation exchange resins, containing carboxylic acid groups or the corresponding salts.
- 3- Strongly anion exchange resins, containing quaternary ammonium groups. Of these, there are two types:
 - a- Type I resins contain trialkyl ammonium chloride or hydroxide and Type II resins contain dialkyl
 - b- hydroxyethyl ammonium chloride or hydroxide.
- 4- Weak anion exchange resins, containing ammonium chloride or hydroxide [Aldrich, 2002].

There are basically three types of operating methods for ion exchangers. They consist of batch, fixed bed and moving bed operations [Bolto and Pawlowski, 1987; Kunin, 1963].

Most ion exchange operations follow the same sequence with certain variation from process to process. These in their normal order are:

- 1- Backwash. The flow of water is reversed to expand the ion exchange resin bed for removal of turbidity and also removes accumulated deposits from the surfaces of the resin.
- 2- Regeneration or brining step. A 10 – 12% solution of NaCl is passed downward through the unit. The regeneration reaction is reversible; the ion exchanger is not permanently changed. The regeneration step makes the resin ready for another cycle of operation.
- 3- Rinse. Excess NaCl is rinsed from the unit with hard water in a downward flow pattern. The softener is then returned to its services cycle [Kirk – Othmer, 1981; Considine, 1974].



STUDYING THE BREAKTHROUGH TIME FOR STRONGLY ACIDIC CATION EXCHANGERS

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ABSTRACT

The aim of this research is to study the breakthrough time for cation exchangers by using a pilot plant of ion exchange and passing water with different concentrations of hardness. The pilot plant consisted of one column containing strongly acidic cation exchanger of styrene divinylbenzene type. The study covered the effects of the flow rate (1.013 – 5.067) L/hr, bed depth (0.1 – 0.5) m, and hardness concentration (200–500) ppm on breakthrough time for cation exchangers. In a column with (2.5 cm in diameter).

Box–Wilson composite ratatable design method was adopted in the designing the experimental work. This method proposed second order polynomial mathematical model and their coefficients are estimated through non – linear regression analysis to correlate the response function (breakthrough time) with the three variables (flow rate, bed depth, and hardness concentration).

الخلاصة

يهدف هذا البحث إلى دراسة زمن الاختراق لمبادلات الأيونات الموجبة من خلال استخدام نموذج ريادي مصغر لمنظومة التبادل الأيوني وإمرار مياه ذات عسرة مختلفة التركيز خلال تلك المنظومة. تتكون منظومة التبادل الأيوني من عمود محشو بمبادلات الأيونات الموجبة قوية الحامضية. شمل البحث دراسة تأثير معدل الجريان (1.013 – 5.067) لتر/ ساعة، ارتفاع الحشوة (0.1 – 0.5) متر، وتركيز العسرة (200 – 500) جزء بالمليون على زمن الاختراق لمبادلات الأيونات الموجبة بعمود نصف قطره (2.5) سم.

استخدمت طريقة إحصائية تعرف بطريقة بوكس ولسن لتصميم التجارب العملية واقتُرحت هذه الطريقة علاقة رياضية متعددة الحدود من الدرجة الثانية وتم إيجاد حدودها بتطبيق طريقة التحليل الانحداري اللاخطي على النتائج العملية لإعطاء النتائج المتوقعة لزمن الاختراق.

KEY WORDS

ion exchange, resin, breakthrough time, hardness, and softener.

INTRODUCTION

Although ion exchange is becoming more and more important in the treatment of water and wastewater, the water softening field still remains as the foremost and largest scale ion exchange operation.