WATER TREATMENT OF COOLING TOWERS BLOWDOWN BY ION EXCHANGE

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ABSTRACT

This work was conducted to study the effect of relevant parameters on the performance of ion exchange process for water treatment, using Doulite C-20 (strong cation) Doulite A-378 (weak anion) in a 0.025 m column.

The effects of conductivity of feed water in the range of (1000-1500 μs/cm), flow rate in the range of (1.2-7 l/h) and bed depth of resin in the range of (50-70 cm) on the breakthrough time and adsorption capacity were studied for ion exchange process. The best operating conditions, which lead to good quantity and quality for water product, are: (1000- 1100 μs/cm) conductivity of feed water, (4-5 l/h) flow rate, and (65-70 cm) bed depth of resin. At these conditions the breakthrough time is (6.51 hr), and the adsorption capacity is (54.193 ml/ml wet resin).

INTRODUCTION

In the ion exchange process, the most common deionization system is the two beds strong acid cation followed by weak base or strong base anion. Ion exchanger is a chemical treatment process used to remove unwanted ionic species from wastewater[1,2]. As the name implies, ion exchange works by exchanging undesirable cations or anions in solution with less harmful ones. 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 [3,4]. The exchange reaction is reversible, and the exchange contaminates can later be removed from the resin, making the resin available for reuse. Ion exchange resins consist of inorganic minerals with a deficit of positive atoms within the crystalline structure, known as zeolites, or synthetic organic polymeric materials that have ionizable functional groups, such as sulfonic, phenolic, carboxylic, amine, or quaternary ammonium. In solution, salts separate into positively charged cations and negatively charged anions. Deionization can reduce the amounts of these ions to very low levels through the process of ion exchange (5,6).

Cations are removed by cation exchange resin. It replaces sodium, calcium, copper, magnesium and other cations with hydrogen ions (H+). This exchange produces acids, which must be removed or neutralized by anion exchange resin. Tow general types of anion resin are used for deionization: weak base resin and strong base resin. Weak base resin adsorbs acids, while strong base resin exchange chloride, sulfate and alkaline anion for hydroxide ions (OH$^-$). The hydrogen ions from the cation exchange process combine with the hydroxide ions from the anion exchange process to form water. Because the deionization process is so effective, the water quality is usually measured by the water's resistance to electric current (in OHM-cm). Apart from theoretical considerations the following factors influences operating capacity, including water composition, ion exchange types and quantities, regeneration levels, flow rates, water temperature, and method of regeneration, i.e., co-flow or counter flow [7,8].

The two most common theories that have been developed to quantitate ion exchange equilibrium are by analogy to a membrane exclusion phenomenon (9).

If treated as a chemical reaction, mass action laws can be used to describe the distribution of ions in the solution and resin phases.

The Donnan equilibrium model describes the behavior of ions based on the unequal distribution of ions across a membrane when an electrolyte solution on one side of the membrane contains ionic species that can not diffuse through the membrane.

However the mass action derivations will give the same equilibrium expression as the membrane theory.

The exchange of cation is usually described by an equation of the following kind

$$bA+a +aZB \rightleftharpoons aB+b +bZA \qquad (1)$$
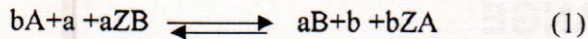
The equilibrium expression for this reaction can be written as:

$$K_B^A = \frac{q_A^b C_B^a}{q_B^a C_A^b} = \frac{(q/C)_A^b}{(q/C)_B^a} \qquad (2)$$

K_B^A is typically called the equilibrium "constant" but in ion exchange it is referred to as the selectivity coefficient and is not actually a constant but depends on experimental conditions. The separation factor is also commonly used to give the preference of a resin for ions:

$$\alpha_B^A = \frac{(q/C)_A}{(q/C)_B}$$

For monovalent ion exchange $\alpha_B^A = K_B^A$, but for multivalent- Mono valent exchange, the two are not equal (1).

The over all exchange process may be divided into five distinct steps:

1. The diffusion of ions through the solution to the surface of the exchange particles (film diffusion).
2. Diffusion of these ions through the gel particle (particle diffusion).
3. The exchange of these ions with those already in the exchanger.
4. Diffusion of these displaced ions through the exchanger.
5. Diffusion of these latter ions through the solution.

Each step of the diffusion, whether in the resin or solution phase, must be accompanied in the presence of an ion of the opposite charge, and for the law of electroneutrality must be obeyed at all times (10).

At concentrations of less than (0.003 M), the diffusion of ions through a film of solution (Nernst film) about each particle is considered to be the rate- determining process, and at concentration above (0.1M), the diffusion of ions throughout the gel particle becomes the rate-determining process [11].

It is now generally accepted that the over all rates of ion exchange reaction are determined by diffusion rates rather than by the actual exchange rates at the exchange site because the latter is fast.

Partial water treatment generally is directed toward purifying the water to the degree that use requires and seldom to complete purification or total removal of all impurities. The treatment of water consists of two processes, water softening and deionization of water (3). The ion exchange water softener is one of the most common tools of water treatment. Its function is to remove scale forming calcium and magnesium ions from hard water.

When hard water is passed through the resin tank, calcium and magnesium ions adhere to the resin, releasing the sodium ions. The resin bead exchange site adsorb sodium ions and displace multivalent cation during regeneration with solution of NaCl (1).

The reaction can be represented by the following equation:

$$2R - Na^+ + M^{++} \rightleftharpoons R_2M^{++} +2Na^+ \qquad (4)$$
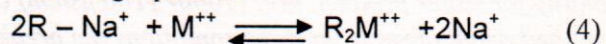
Deionization uses a two - stage process to remove virtually all-ionic material in water. Two types of synthetic resins are used (12):

1. Cation deionization resins (hydrogen cycle) release hydrogen (H+) in exchange for cation such as calcium, magnesium and sodium.
2. Anion deionization resins (hydroxide cycle) exchange hydroxide (OH-) ions for an ions such as chloride, sulfate and bicarbonate. The displaced H+ and OH- combine to form H2O.

The process is represented by the following equations :

$$R-SO_3 + NaCl \rightleftharpoons RSO_3Na+HCl \qquad (5)$$
$$R-NH_3 OH + HCl \rightleftharpoons R-NH_3 Cl +H_2O \qquad (6)$$
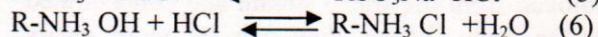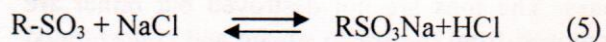
EXPERIMENTAL WORK

The present experimental investigation study was directed to study the performance of the ion exchangers towards salt water from cooling tower blowdown in one of the factories of the State Company for Vegetable Oils.

The present work was initiated to study the effect of changing the conductivity of feed water, flow rate and bed depth on the operation of ion exchange.

Then, the adsorbed ions are concentrated in small volumes by regenerating the cation exchanger and the anion exchanger using HCl and NaOH solutions respectively.

Conductivity of feed water ranged between 1000 to 1500 µs/cm .Flow rate ranged between 1.2 to 7 l/h. Bed height of cation exchanger

ranged between 50 to 70 cm . And Bed height of anion exchanger is 70 cm.

The experiments were started and continued until breakthrough point that was already decided to be at 40 µs/cm conductivity, was detected. The average conductivity of the total resulted deionized water from each run ranged between 10 to 17 µs/cm. The run was continued until full exhaustion point was detected where output concentration equals to input concentration. A factory sample of salt water was found to have TDS content equivalent to conductivity of 1300 µs/cm. Monitoring the TDS concentration in the product water was carried out by measuring the electric conductivity of this effluent.

Chemicals Used

The following chemicals were used:

1. 4% HCl solution for regeneration of cation exchanger.
2. 4% NaOH solution for regeneration of anion exchanger.
3. Doulite C-20 (strong cation exchanger).
4. Doulite A-378 (weak anion exchanger).

Equipment and Measurement Devices

A schematic diagram of the equipment is presented in fig. (1) which consists of the following parts:-

1. QVF glass vessels with a capacity of 30 L, 10 L and 10 L were used as a feeding vessel, regenerating vessel for the cation exchanger and regenerating vessel for the anion exchanger respectively.
2. Glass column of 140cm long and 2.54cm diameter.
3. Plastic valves to control opening and closing, direction into column to another.
4. A centrifugal pump used for pumping water from the feed tank to the system. The specifications of the pump are as follow:-

Capacity	3-9.1 l/min
Head	1.5-6.1 m
Supplied voltage	220-240 V
Power	60 W

5. The rotameters to measure the volumetric flow rate of feed solution (0.5 to 10 l/h).
6. The conductivity meter used to measure the conductivity in the feed stream and in the out stream.

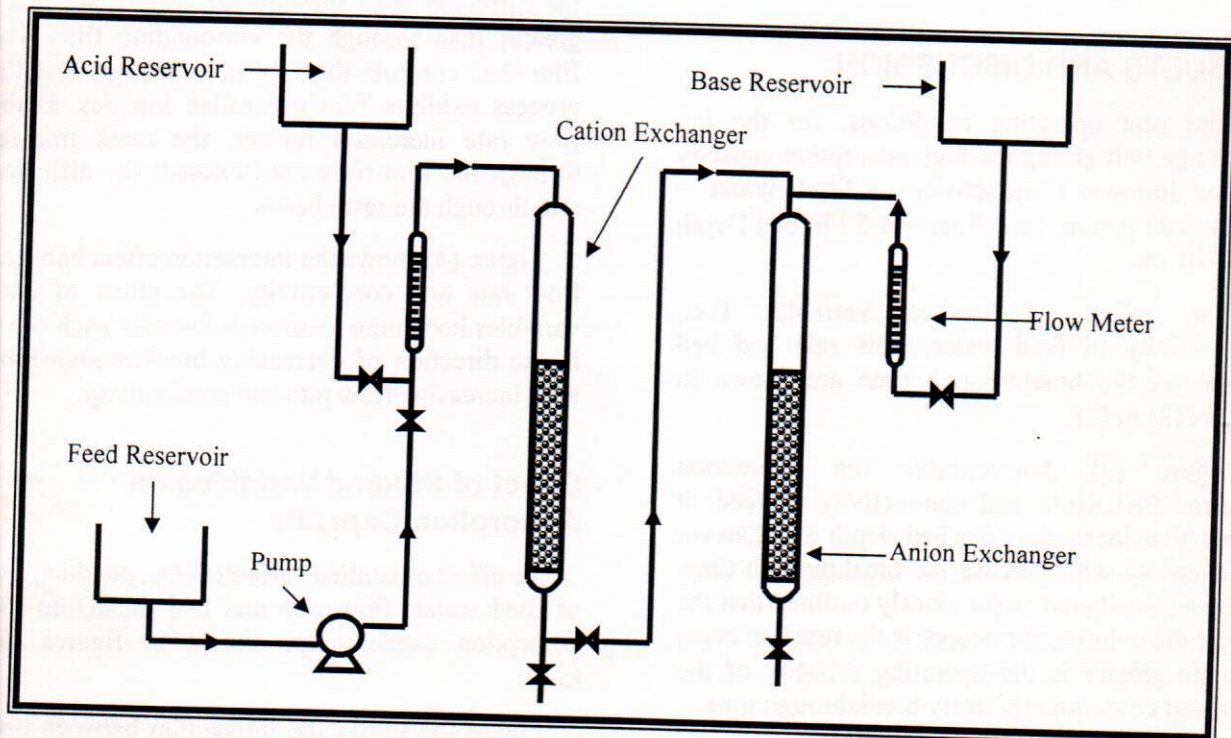 | | | |
    |---|---|---|
    | Type | = | KENT, 74435 |
    | Range | = | $0 - 45 * 10^3$ µS/cm |
    | Power supply | = | 9 Volt |

Fig. (1) Schematic Diagram of Pilot Unit

Experimental Procedure

Soaking the resin before adding it to the column to allow it to reach its hydrated volume. The two columns were soaked with deionized water, columns are packed with strong acidic cations exchanger and weakly basically basic anion exchangers respectively. The ionic exchanger in columns were washed upwards with the 50-100% bed expansion for 5 to 15 minute using distilled water.

Regeneration of the cation exchanger was carried out by acid solution of 4% HCl. The acid solution flowed downflow by gravity from tank into column. This regenerates the resin at a flow rate of 4-bed volume/h. for at least 45 minutes of contact time. Regeneration of the anion exchanger was carried out by base solution of 4% NaOH. The base solution flowed downward by gravity from tank into column. This regenerates the resin at a flow rate of 4-bed volume/h. for at least 45 minutes of contact time.

Deionized water is pumped downward into column with a flow rate of 4-bed volume/h. the slow rinsing step lasted for 15 minutes. Deionized water is pumped downward into column with a flow rate of 8-bed volume/h. the fast rinsing step lasted for 30 minutes.

RESULTS AND DISCUSSION

The best operating conditions, for the ion exchange unit giving the high adsorption capacity are as follows: Conductivity of Feed Water = 1000-1100 µs/cm, flow Rate = 4-5 l/h, bed Depth = 65-70 cm

The effect of studied variables (i.e., conductivity of feed water, flow rate and bed depth) on the breakthrough time are shown in figures (2) to (4).

Figure (2) demonstrates the interaction between bed depth and conductivity of feed. It seems that increasing the bed depth at whatever conductivity will increase the breakthrough time. This was attributed as previously outlined that the longer the column, the deeper is the reaction zone, and the greater is the operating capacity of the resin and consequently lately breakthrough time.

With higher conductivity of total dissolved solids, the conductivity of ions in solution increases that increases the mass transfer rate through the film until it exceeds the diffusion rate through the resin beads. Then diffusion through the resin becomes the controlling factor and the system is said to exhibit particle controlled kinetics, which is slower process. This condition means that the leakage curve is spread out over deeper reaction zone. If this condition is happened it leads to shorter exhaustion time and lower operating capacity.

Figure (3) shows the interaction between flow rate and bed depth. Both variables tend to effect the breakthrough time in opposite direction but it seems that the flow rate has the most significant effect on breakthrough time in comparison to bed height.

If the flow rate is low enough, equilibrium is established as the solution reaches a new layer of the resin that means the wave front is only slightly diffuses as a result of each successive layer of resin being almost completely exhausted before leakage occurs. As flow rate increases, equilibrium is no longer reached and the exhaustion curve is spread out over deeper reaction zone which has a smaller operating capacity and earlier break through point.

Furthermore, the curve tends to flatten (i.e., no further tendency to decrease) at higher flow rate. This was attributed that if the flow rate is slow, the diffusion rates through the resin mass much greater than through the surrounding film. The film thus controls the rate of exchange, and the process exhibits film controlled kinetics. If the flow rate increased further, the mass transfer through the film rises until exceeds the diffusion rate through the resin beads.

Figure (4) shows the interaction effect between flow rate and conductivity. The effect of both variables had come in accordance with each other in the direction of decreasing breakthrough time with increasing flow rate and conductivity.

Effect of Studied Variables on Adsorption Capacity

The effect of studied variables (i.e., conductivity of feed water, flow rate and bed depth) on the adsorption capacity are shown in figures (5) to (7).

Figure (5) shows the interaction between bed depth and conductivity. At low conductivity, higher adsorption capacity was noticed and the

adsorption capacity was increased with longer bed height. The effect of conductivity on adsorption capacity shows lower adsorption capacity with higher conductivity. This is attributed to higher mass transfer rates through the film until it exceeds the diffusion rate through the resin beads and consequently the leakage curve is spread out over deeper reaction zone that means shorter exhaustion time and lower operating capacity.

The adsorption capacity increased with longer bed height. It was simply observed that longer column means greater adsorption capacity, which is simply attributed to a deeper reaction zone.

Figure (6) demonstrates the interaction between flow rate and bed depth. The effects of flow rate on adsorption capacity shows lower adsorption capacity with higher flow rate. This is attributed to higher mass transfer rate through film and consequently the leakage curve is spread out over deeper reaction zone that might shorten exhaustion time and lower adsorption capacity.

At higher values of flow rate, large variation in adsorption capacity with bed depth was noticed in comparison with the lower values. However, at low values of flow rate, higher adsorption capacity was observed in comparison with higher values. This observation had been already been noticed and explained according to slightly diffused wave front that results in each successive layer of resin, at low flow rate, being almost completely exhausted before leakage occurs.

As flow rate increases, equilibrium is no longer reached and the exhaustion curve is spread out over deeper reaction zone which shows lower adsorption capacity. At longer bed depth, higher adsorption capacity was monitored with increasing flow rate. Whereas, at shorter bed depth, lower adsorption capacity with increasing flow rate was observed. In other words, at lower bed depth leakage has occurred earlier that resulted in lower adsorption capacity.

Figure (7) demonstrates the interaction between flow rate and conductivity. Here, the adsorption capacity initially increases slightly to a high value of flow rate (approx. 4 l/h) then decreases with increasing flow rate at the limit of conductivity (i.e., 1000 μs/cm). The same explanation as that given above may be used here.

CONCLUSIONS

The following conclusions can be pointed out from this study:
1. The three variables:- conductivity of feed water, flow rate and bed depth effect the breakthrough time in the order: Flow rate > bed depth > conductivity of feed water. And effect of the experimental variables on the adsorption capacity is in the order: Bed depth > flow rate > conductivity of feed water

2. Higher concentration of total dissolved solids leads to higher concentration of ions in solution that results in higher mass transfer rate through the film until it exceeds the diffusion rate through the resin beads and consequently the system exhibited particle controlled kinetics which means deeper reaction zone (a condition that leads to shorter exhaustion time and lower operating capacity).

3. The best operating conditions for ion exchange pilot plant are (1000-1100 μs/cm) conductivity of feed water, (4-5 l/hr) flow rate, and (65-70 cm) bed depth. At these conditions the breakthrough time is (6.51 l/hr) and the adsorption capacity is (54.193 ml/ml wet resin).

NOMENCLATURE

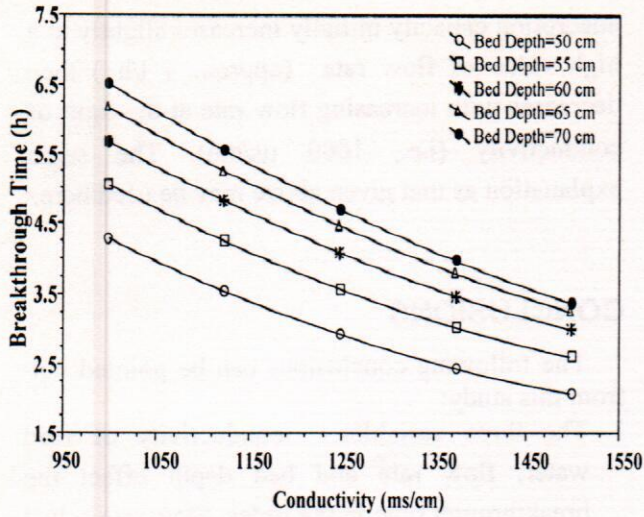| Symbol	Definitions	units
A	Ion in solution	-
B	Ion attached to the resin	-
K_B^A	Equilibrium constant	-
Q	Solid-phase ionic concentration	meq/gram
Z	Resin	-
Greek symbols		
α_A^B	Separation Factor	-

Fig. (2) Effect of Conductivity on Breakthrough Time
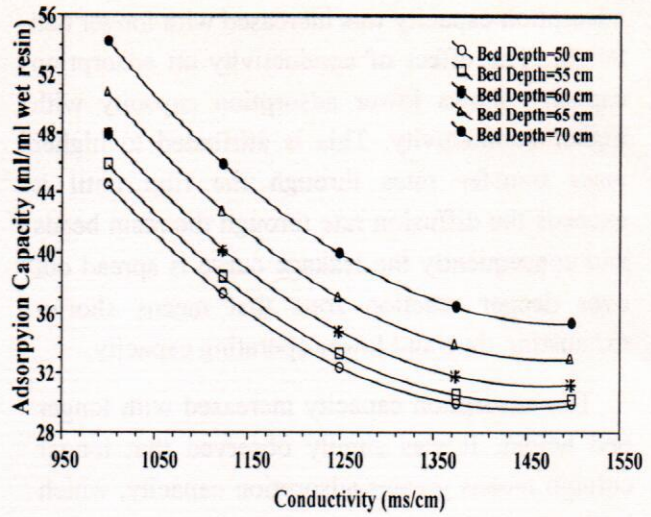at different Bed Depth at a Flow Rate of (4.7 l/h)

Fig. (5) Effect of Conductivity on Adsorption Capacity
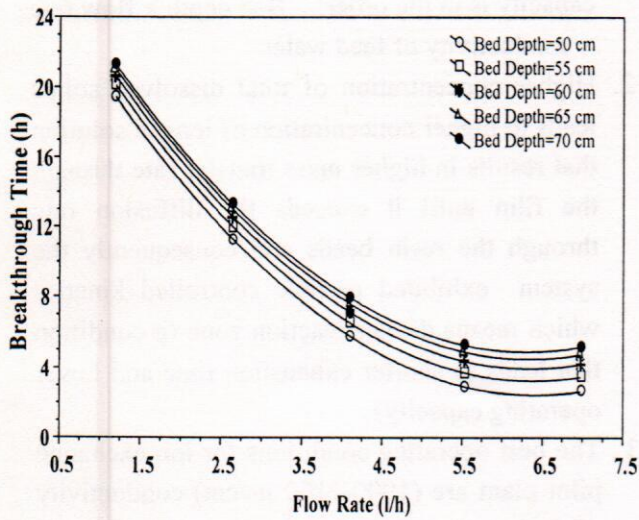at different Bed Depth at a flow Rate of (4.7 l/h)

Fig. (3) Effect of Flow Rate on Breakthrough Time at
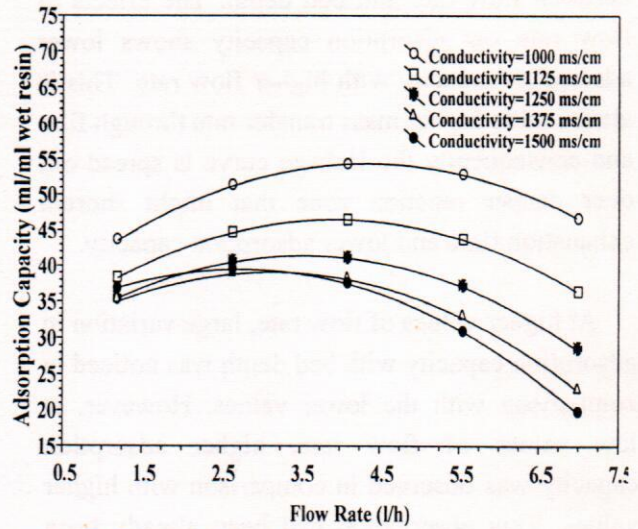different Bed Depth at a Conductivity of (1000 μs/cm)

Fig. (7) Effect of Flow Rate on Adsorption Capacity at
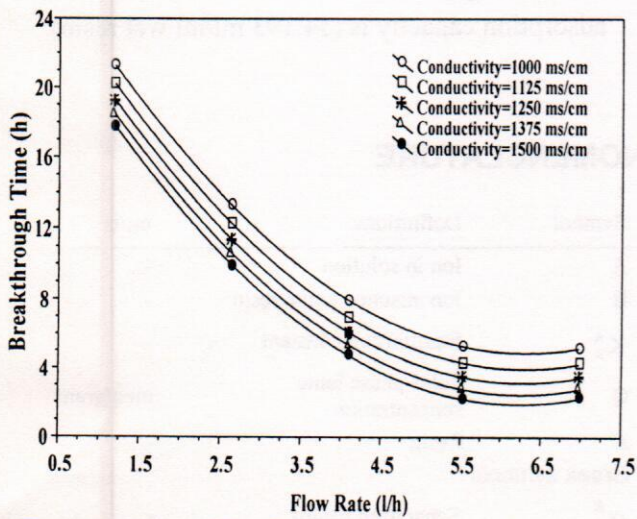different Conductivity at a Bed Depth of (70 cm)

Fig. (4) Effect of Flow Rate on Breakthrough Time at
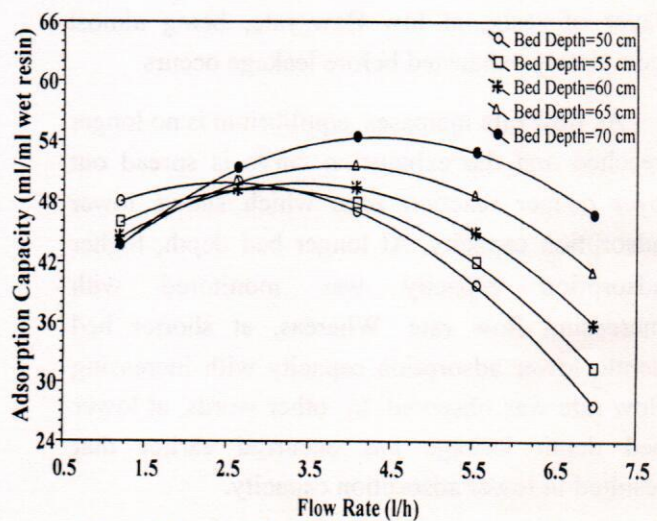different Conductivity at a Bed Depth of (70 cm)

Fig. (6) Effect of Flow Rate on Adsorption Capacity at
different Bed Depths and at a conductivity of (1000 μs/cm)

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