

Experimental study on Ion Exchange Rate of Calcium Hardness in Water softening process Using Strong Acid Resin DOWEX HCR S/S

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Abstract

Water Softening process is one of the techniques used to minimize the hardness of drinking water by exchanging the present of hardness ions especially Mg^{+2} and Ca^{+2} ions by Na^{+1} ion. For this purpose, strong cationic resin can be used, which is efficient in separation method applied in water treatment. The aim of the present work was to determine the efficient flow of softening column (softener), and to specify the best properties of resin which included the particle size at constant ambient temperature (27⁰ C) and pH = 7.2 . This study was concentrated on the behavior of Ca^{+2} ion by passing $CaCl_2$ solution with certain concentrations over cationic resin of type (DOWEX HCR S/S) to replace the Ca^{+2} ion by Na^{+1} on in feed solution to produce NaCl. Process parameters investigated were: concentration, flow of feed , the size of a certain type of cationic resin , the effect of superficial velocity rate and the diameter of resin bed.

Nomenclatures:

A	cross sectional area of column in m
At.wt	Atomic weight of calcium (40.078 g/mol)
C	total ionic concentration of water, eq/L
C_1	inlet concentration (g /L) of Ca^{++}
C_i	Initial concentration of $CaCl_2$
C_0	outlet concentration (g /L) of Ca^{++}
C_{Na}	sodium concentration in water , eq/L
$K_{Ca/Na}$	selectivity coefficient
M.wt	Molecular weight of $CaCl_2$ (110.98 g/mol)
q	total exchange capacity on resin, eq/L
q_{Na}	sodium concentration in resin , eq/L
Q	flowrate in m ³ / hr
R	total ion exchange efficiency on resin, %
X_{Na}	equivalent fraction of sodium in resin , q_{Na}/q
y_{Na}	equivalent fraction of calcium in resin , q_{ca}/q

v	Volume of solution (L)
V	interstitial velocity m/hr
V_s	superficial velocity m/hr
W	weight of $CaCl_2$ (g)
η	exchanging efficiency
$\alpha_{Ca/Na}$	separation factor

1. Introduction

The hardness of water causes many big problems in industry and health. The softening process used to decrease the hardness of water includes several techniques, the most efficient and well qualified is ion exchange process [1]. Ion exchange has been used in industry since 1910 with introduction of water softening. Today most ion exchange resins basis are styrene and divinylbenzene resins which is then sulfonated. As resins are ready for use, sodium ions generated from salts will pass through the resin replacing the hydrogen ions with sodium ions. [2]

Ion exchange reaction is an irreversible stoichiometric reaction interchange of ions between a solid phase and a liquid phase. The ion exchange is usually insoluble in the medium in which the exchange is carried out. Ion exchange has been used frequently as an economical and convenient separation method to produce pure water.[3]

The ion exchange reaction is described as below :

$$2\check{R}-Na(\text{resin})+Ca^{++}(\text{solution})\rightarrow 2 Ca-\check{R}(\text{resin})+2 Na^{+}(\text{solution}) \quad \dots (1)$$

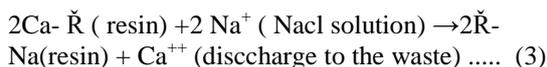
\check{R} represent the sulphonic group.

A chemical equilibrium is established between the ion exchange resin and solutions in contact with the resin. This is expressed by the standard equilibrium mass action expression [4] :

$$K = \frac{[Na^{+}]^2}{[Na^{+}]_R^2} \cdot \frac{[Ca^{++}]_R/2}{[Ca^{++}]/2} \quad \dots (2)$$

The reaction takes place in the upper layer of resin bed in the exchange column .So, the active resin will be decreased and exhausted upon moving down the resin bed. In the intermediate layer of bed mixing occurs between active and exhausted resins. The resin exhausted completely in the lower layer of resin bed.

The regeneration reaction can be represented by the reverse reaction of the softening reaction as



To guranty a complete active sample of resin, the regeneration should be carried out after each test run .The resin is regenrated by sufficient sodium chloride solution with concentraion ranged 8-10 % . The conventional quantity of salt is 200 g per liter of resin. After regeneration the rsin should be rinsed carefully by disttiled water to remove all salt traces[5].

The range of solutions chosen with Ca⁺⁺ concentration is between100-1000 ppm, which covers the high level of hardness. According to WQA,s level of hardness guidlines are as follows [6] :

- Less than 17.1ppm as CaCO₃ (6.84 ppm as Ca⁺⁺) is considered soft.
- 17.1-60 ppm as CaCO₃(6.84 –24) ppm as Ca⁺⁺ is considered slightly hard.
- 60-120 ppm as CaCO₃(24-48) ppm as Ca⁺⁺ is considered moderatly hard.
- 120-180 ppm as CaCO₃ (48 -74) ppm as Ca⁺⁺ is considered hard.
- Greater than 180 ppm as CaCO₃ (74 ppm as Ca⁺⁺) is considered very hard.

Many previous studies have considered the effect of operating conditions on the softening process.

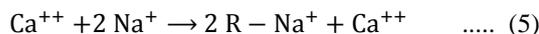
Ghanim et al. [7] illustrated the relation between the flow rate of water, inlet concentration and temperature of softener by second order nonlinear empirical model.

Zaganiaris , [8], improved the relation between concentration of salts in feed solution (hardness) and separation factor. He studied the distribution of ions between solution phase and resin phase which is nominated by separation factor $\alpha_{i/j}$ and defined :

$$\alpha_{i/j} = \frac{\text{Distribution of ion i between phases}}{\text{Distribution of ion j between phases}} \dots (4)$$

Bodgan, et al. [9] studied the effect of several operational conditions including pH and initial concentration of Ca⁺⁺ on ion efficiency of cationic resin type purolite C100.

To understand the affinity factors should be study the separation factors of Ca⁺⁺ and Na⁺ which are related strongly by affinity, equation(1) can be rewritten in simplified shape:



According to eqn.(3), the separation factor ($\alpha_{Ca/Na}$) can be written :

$$\alpha_{Ca/Na} = \frac{(Y_{Ca}/X_{Ca})}{(Y_{Na}/X_{Na})} = \frac{(Y_{Ca} \cdot X_{Na})}{(X_{Ca} \cdot Y_{Na})} \frac{(q_{Ca}/q)(C_{Na}/C)}{(C_{Ca}/C)(q_{Na}/q)} \dots (6)$$

$$\alpha_{Ca/Na} = K_{Ca/Na} (q \cdot Y_{Na}) / (C \cdot X_{Na}) \dots (7)$$

Hence $K_{Ca/Na}$ is selectivity coefficient and is defined as:

$$K_{Ca/Na} = (q_{Ca} \cdot C_{Na}^2) / (C_{Ca} \cdot q_{Na}^2) \dots (8)$$

Equation (8) indicates clearly that as concentration (C) is increased the separation factor ($\alpha_{Ca/Na}$) decreases.

Coca et al. [10], investigated the removal of Ca⁺⁺ from juice by using Lewatit S 8528 in the acidic form is a feasible alternative to the classical strong cation exchange resins, providing calcium removal efficiencies higher than 80%.

A.A.swelam et al. [11], showed the ion adsorption increased with the increased with increasing of initial concentration by using cationic resin type resinex K -8H .

Aruop .K.SenGupta [12], described the influence of particle size of resins for both uses , industrial grade and chromatograph grade .He improved the relation between particle size with diffusivity and mass transfer coefficient .

Xie and Huang [13], studied the rate of reaction on resin particles surface for different particles sizes of resin and showed that the rate of reaction increased with decreasing particles size.

2. Experimental work

The cationic resin DOWEX HCR S/S was used,the specifications of resin fixed in Table.1. The particle size ranged from 0.3 - 1.3 mm, two samples of these types were prepared by screening . The grain sizes were 1.1-1.2 mm and 0.5-0.6 mm for the first and second samples respectively..

Table. 1 : Resin Type DOWEX HCR S/S specifications [14]

	Sample 1	Sample 2
Type	Styrene divinylbenzene copolymer	Styrene divinylbenzene copolymer
Code	DOWEX HCR S/S	DOWEX HCR S/S
Physical form	Amber beads	Amber beads
Functional group	Sulfonic acid	Sulfonic acid
Ionic form	Na ⁺	Na ⁺
exchange capacity	1.9 eq/L	2.2 eq/L
Shipping weight	800 g/L	850 g/L
Particles size	1.1 mm	0.5 mm
Specific gravity	1.3	1.3

2.1 Exchange unit:

Laboratory set – up shown in Fig.1 is manufactured By Gunt. All experimental test carried out in laboratories of Chemical

Engineering Department –Alnahreen University. The exchanging of Ca⁺⁺ ions by Na⁺ ions was carried out by using small pilot ion exchange plant model CE300

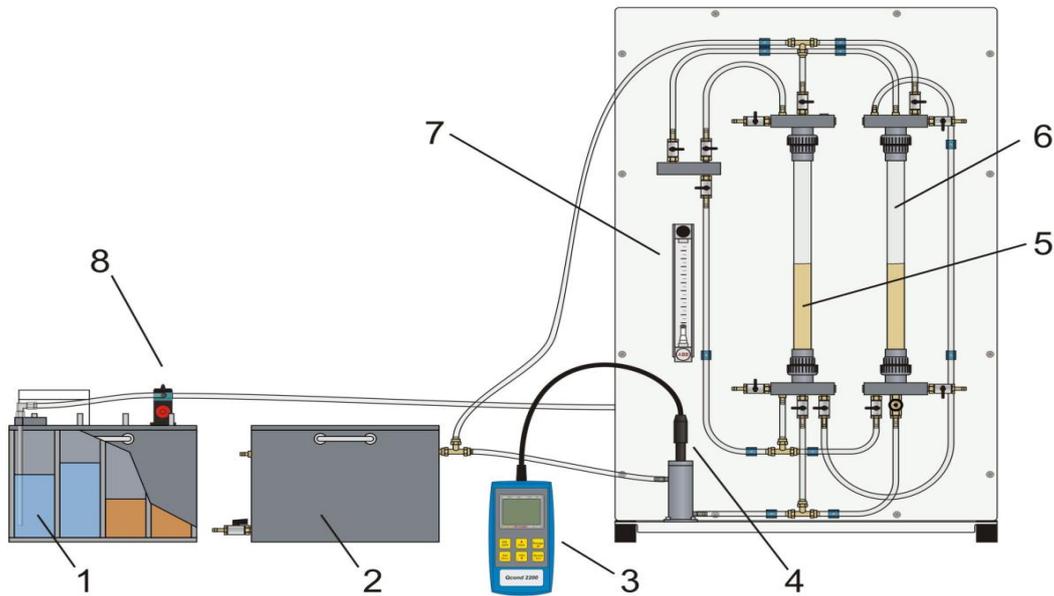


Figure 1: Laboratory set - up.

- 1- Supply tank with feed solutions. 2- collecting tank 3- Conductivity meter 5- container pipe for ion exchange resin sample(1) 6- container pipe for ion exchange resin sample(2)
- 7 -Rotameter 8- feed pump

The unit contained two glass columns filled with strong cationic resin type-DOWEX HCR S/S. The specifications of both resins types used are identical, except the grain size to achieve different superficial velocities.

The dimensions of column are length is 320 mm, O.D is 25 mm and I.D is 21.2 mm. The CaCl₂ solution was pumped to column by small pump. The capacity of pump was from 0-300 ml / min, with constant pressure. The solution was pumped through small plastic hose. The flow rate was measured by rotameter with range from 20–260 ml / min. The feed solution was prepared in the PVC plastic tank with capacity 20 liter. The conductivity of outlet from exchange column was measured by online conductivity- meter.

Two particle sizes of resin were used to investigate the effect of particle size on the rate of ion exchange softening. The resins were screened to separate two sizes. The first ranged from 1.0 to 1.3 mm and the second ranged from 0.4 to 0.6 mm.

2.2 Solutions Preparation :

The feed solutions of CaCl₂ were prepared in 100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ppm. by dissolving different weights of CaCl₂ powder in 4 Litre of distilled water. The

CaCl₂ weights were calculated by using following equation [15]:

$$W = v \times C_i \times \frac{M.wt}{At.wt} \dots (9)$$

3. Calculation:

a. The superficial velocity was calculated via[16]:

$$V_s = \epsilon V \dots (10)$$

Where ϵ is the void fraction in a packed bed and is defined as:

$$\epsilon = \frac{\text{volume of void in bed}}{\text{total volume of bed(voids + volume of solids)}} \dots (11)$$

And V_s is the interstitial velocity of water on cross section of the empty column represented by:

$$V = \frac{Q}{A} \dots (12)$$

b- The exchanging efficiency (η) is an important index to evaluate the performance of the process, and is given as[17]:

$$\eta = \frac{C_0 - C_1}{C_0} \times 100 \dots (13)$$

c- The remaining concentration of Ca⁺⁺ ion (C_1) in solution mixture at the outlet can be calculated by using complexmetric methods titration with EDTA[18],

This method determines the remaining Ca^{++} content which has not been exchanged with Na^+ to produce $NaCl$.

The analyses was carried out by titration with ethylenedi-aminetetraacetic acid (EDTA) using Patton and Reeder's (PR) as indicator to provide an end-point signal[19].

For the titration, the indicator was added to the sample solution which contains the remaining calcium ions and form pink/ red calcium ion-indicator complex (Ca-PR). This solution is titrated with EDTA (0.01 M). The end point is attained when solution turns blue, indicating that Ca-PR complex has been completely replaced by the calcium ion-EDTA complex and the PR indicator reverts to its blue color [20].

The reaction is:



Note: Ca - PR is pink/red and PR is blue.

For low concentration of Ca^{++} , the ratio Ca^{++} : EDTA in case using EDTA solution (0.01 M) will be 1:1[21]. For high concentrations of Ca^{++} EDTA solutions (0.1, 0.2 M) was used.

4. Results and discussion

4.1 Effect of superficial velocity on exchanging efficiency (Purification efficiency)

The exchange efficiency (η) is an important index to evaluate the performance of the process, and is given by equation (13).

The rate of exchange at constant concentration varies with the change in superficial velocity for all ranges of concentrations. Figure 2 shows that exchange efficiency decreases with the increasing of superficial velocity. It indicates that at low concentrations, the effect of superficial velocity is lower than in high concentrations. At low concentrations the availability of places on the resin surface which are ready to exchange Ca^{++} ions by Na^+ ions with respect to the Ca^{++} ion number are more than in case of high concentrations[22].

The effect of superficial velocity on exchanging efficiency at high concentration appeared clearly compared with low concentrations. The decrease of superficial velocity will give longer retention time of Ca^{++} ions between resins particles and more exchanging possibility with Na^+ [23].

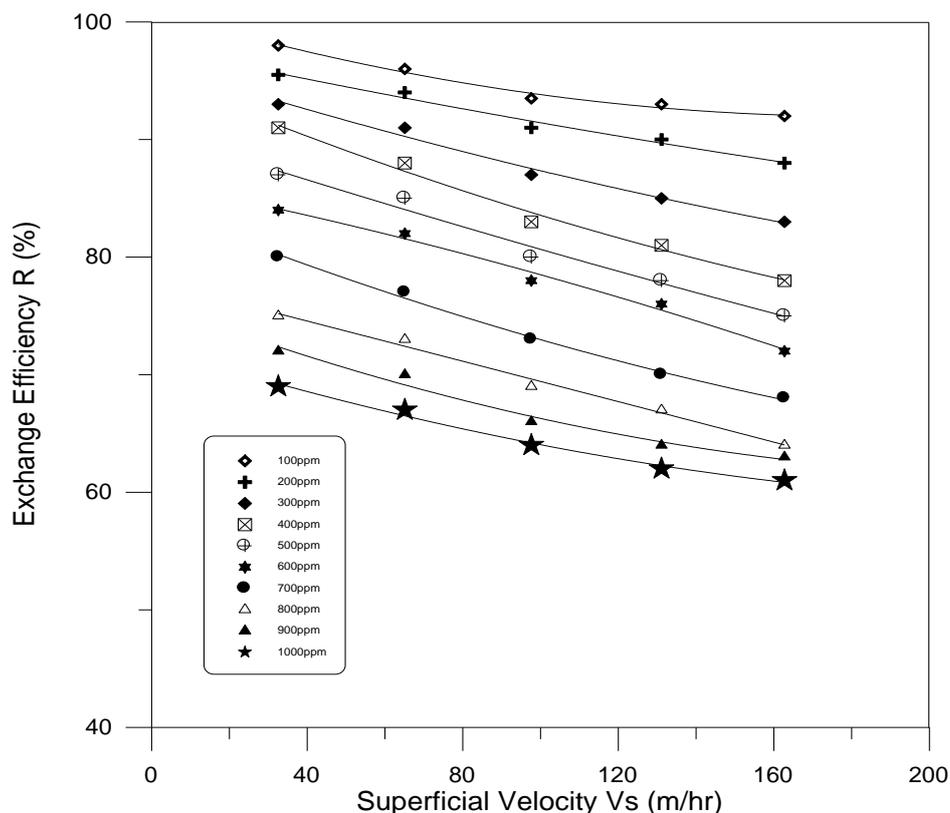


Figure 2: Effect of Feed concentration on exchanging efficiency

4.2. Effect of Feed concentration on exchange efficiency

The increase of Ca^{++} concentration in feed solution decreases the exchange efficiency as shown in Figure 3. Many factors work together in different directions but the result will decrease the exchange efficiency. These factors can be described as follows, the increases of concentration of Ca^{++} in feed solution will increase the driving force of Ca^{++} between the bulk and surface of exchange resin. Moreover, another driving force will be generated by the releasing of Na^+ ion on the surface resin particles

to the bulk of solution. Both ions movement of Ca^{++} and Na^+ in opposite directions will decrease exchange efficiency. The second factor is cation exchange which can only take place efficiently because the cation exchange resin has a higher affinity for the calcium ions than for sodium [24]. The resin prefers calcium over sodium. The result of the softening process is not a net removal of the hardness ions from water, it is the replacement of hardness ions by sodium ions[25]. The salinity of the water has not changed, only the constituents of the salinity are different at the end of the softening process [26]

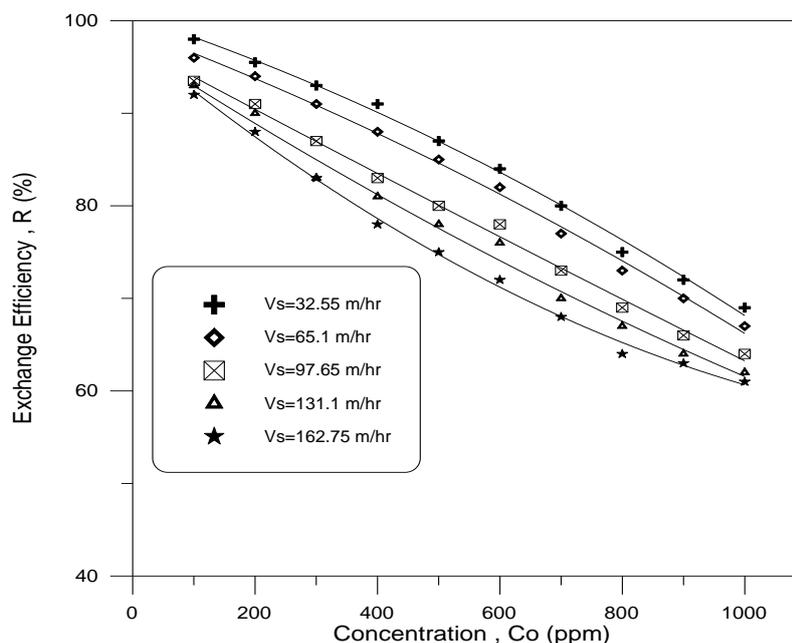


Figure 3: Effect of feed concentration on exchanging efficiency

The experimental results of sample 1 for the effect of superficial velocity and feed

Concentration on exchange efficiency are shown in table .

Table 2: Experimental results for sample 1(resin grain size=1.0 - 1.3 mm)

Run No.	Input solutions		Output solutions									
			Flow rates ml / min									
	C ₀	Concn. By wt. %	Flow:20 ml/min		Flow:40 ml/min		Flow:60ml/min		Flow:80ml/min		Flow:100 ml/min	
V = 12.5 m/hr v _s =32.55 m/hr			R	V = 25 m/hr v _s = 65.1m/hr	R	V = 37.5 m/hr v _s = 97.65 m/hr	R	V = 50 m/hr v _s = 131.1 m/hr	R	V = 62.5 m/hr v _s =162.75m/hr	R	
1	100	0.01	2	98	4	96	6.5	93.5	7	93	8	92
2	200	0.02	9	95.5	12	94	18	91	20	90	24	88
3	300	0.03	21	93	27	91	39	87	45	85	51	83
4	400	0.04	36	91	48	88	68	83	76	81	88	78
5	500	0.05	52	87	75	85	100	80	110	78	125	75
6	600	0.06	96	84	108	82	132	78	144	76	168	72
7	700	0.07	140	80	161	77	189	73	210	70	224	68
8	800	0.08	200	75	217	73	248	69	264	67	288	64
9	900	0.09	252	72	270	70	306	66	324	64	333	63
10	1000	0.1	310	69	330	67	340	64	380	62	390	61

4.3. Effect of resin particles size on exchange efficiency

Figure 4 shows the effect of particle size on ion exchange efficiency (R) for inlet concentration of Ca⁺⁺ 500 ppm and 1000 ppm.

The figure shows that as particle size decreased, the void age between the resin

particles decreased and the superficial velocity will be increased and surface area will be increased too .The decrease in particle size will lead to increase the contact time between the fluid and resin particles and give much time for ions species to exchange with resin and vice versa[27].

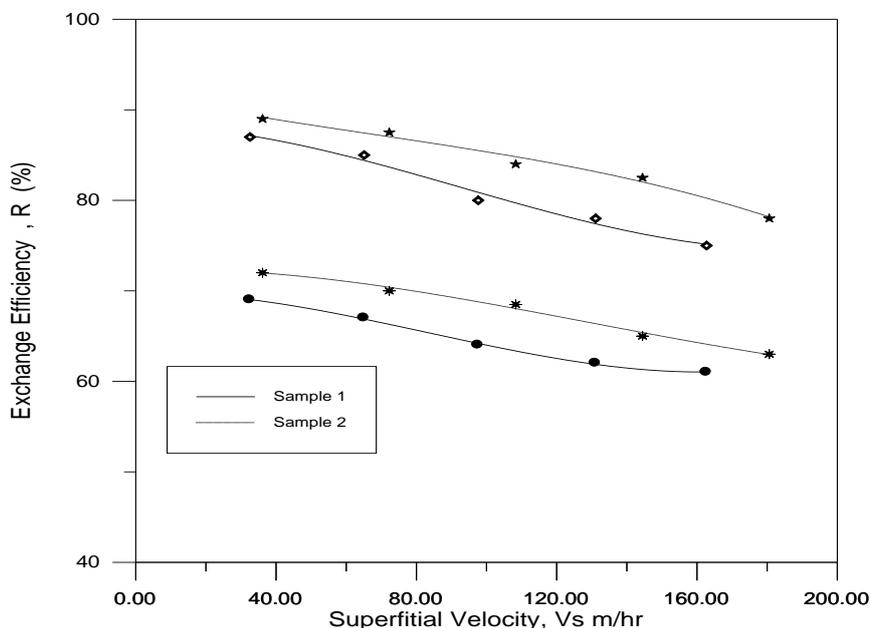


Figure 4: Effect of grain size on exchange efficiency

The experimental results of sample 2 for the effect of particles size on exchange efficiency are shown in table .3.

Table 3: Experimental results for sample 2 (resin grain size=0.5 – 0.6 mm)

Run No.	Input solutions		Output solutions									
			Flow rates ml / min									
	C ₀	Concn. By wt. %	Flow:20 ml/min		Flow:40 ml/min		Flow: 60 ml/min		Flow:80 ml/min		Flow:100 ml/min	
V = 12.5 m/hr v _s =36.12 m/hr			R	V = 25 m/hr v _s = 72.24 m/hr	R	V = 37.5 m/hr v _s =108.36 m/hr	R	V = 50 m/hr v _s = 144.48m/hr	R	V = 62.5 m/hr v _s = 180.6m/hr	R	
1	500	0.05	55	89	62.5	87.5	80	84	87.5	82.5	110	78
2	1000	0.1	280	72	300	70	325	68.5	350	65	270	63

5. Conclusions

The following conclusions can be drawn from this study:

1. The superficial velocity affects the ion exchange efficiency. As superficial velocity increases the exchange efficiency decreases, due to the decrease in contact time between the feed solution and resin particles surfaces.
2. It is very clear that the ion exchange efficiency was increased as concentration in feed water increased. Although, the

Increases in concentration of feed solution will increase the driving force of

exchange with particles surfaces, but the space in particles surfaces will be limited toward the increasing of concentration .

3. The decreases in particles size increases the superficial velocity and surface area of resin which is available for ion exchange. It can be seen that effects are relatively higher than that of the increase in the superficial velocity only.

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دراسة العوامل المؤثرة على معدل ازالة العسرة لأيون الكالسيوم في عملية التبادل الايوني باستخدام الراتنج نوع DOWEX HCR S/S

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الخلاصة

يهدف البحث الى دراسة بعض الظروف التشغيلية المتغيرة لوحدات ازالة العسرة للماء في وحدات التبادل الايوني من خلال استعمال الراتنج الكاتيوني الحامضي القوي (الموجب) نوع DOWEX HCR S/S وقد تمت دراسة بعض الظروف والتي تتضمن سرعة الماء البينية داخل حبيبات الراتنج , تركيز ايون الكالسيوم في الماء الداخل الى وحدة ازالة العسرة وكذلك على الحجم الحبيبي للراتنج. وقد تم في هذا البحث تحديد المسارات التشغيلية عند تغيير الظروف التشغيلية المشار اليها اعلاه عند درجة حرارة الطقس الثابتة (27⁰ م) والدالة الحامضية (pH=7.2) مما يساعد على تثبيت المواصفات الاولية المطلوبة عند تصميم اي وحدة تبادل ايوني وتحديد افضل الظروف التشغيلية لتحقيق الطاقة الانتاجية المطلوبة لوحدات ازالة العسرة.