

Review Article

Parametric Studies of Economical Expect on Desalination Plant Hardness Removal via Resin

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Abstract

Presence of high amount of calcium and/or magnesium makes the water hard as these ions in water react with other chemical agents and constituents of metallic plumbing etc. The process accelerates in the presence of heat. It decreases the efficiency of the unit operation due to the formation of scales. Hence, scaling is the main issue for which hard water is required to be treated or polished. De-mineralized water finds wide application in the fields of steam generation plant, high-pressure boiler feed, power-production plant, process plant, cooling systems, steel mills, refineries, petrochemical complexes, hydrometallurgical, metals finishing etc. The high-purity water from a de-mineralized plant is typically used in computer chip, micro-electronics, semiconductor industries.

Keywords: *hardness removal, poly (acrylamide carboxylic acid) or PAC, scaling, calcium, resin, effluent, parametric studies.*

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Introduction

Safe drinking water following prescribed limit of total dissolved solids as 500 mg/l as per IS and WHO is becoming scarce and hence we need to reuse and re-circulate the water. An amount of 1.0 g calcium/day is considered safe and though [1] calcium has less toxicity, persons who consume more than 4.0 g calcium/day run a risk of hyperparathyroidism-tumor in parathyroid gland, cancer, etc. Similarly low level of calcium may cause kidney stones etc. [2, 3]. Hence, an optimization of calcium content is required for potable water. Although calcium is crucial for bones formation in skeletal living beings, presence of the

element in water is considered as hard, as it reacts with other chemical agents and deteriorate the properties of constituents of metallic plumbing etc. [4]. The process accelerates in presence of heat, therefore decrease efficiency of the unit operation due to the formation of scales [5]. Scaling can be overcome by using Ion Exchangers through the process of softening. Softening of water is the exchange of the hardness producing cations (preferably Ca^{++} , Mg^{++} etc.) with Na^+ or H^+ ion [6–8]. A schematic view has been depicted below.

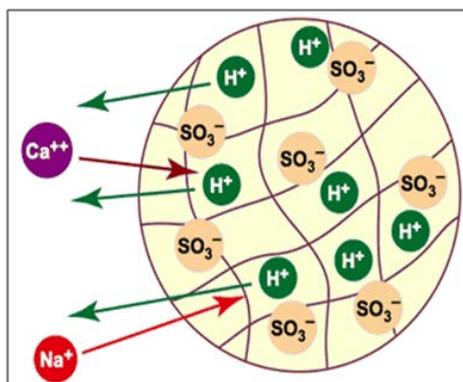


Fig. 1: Decationisation (All Cations Replaced by H^+ Ion).

The cation exchange reactions will be:



After ion exchange, the functional groups capture M^{+n} (Ca^{++} or Mg^{++}) and Na^+ or H^+ ions are released into matrix. Based on this, a novel three dimensionally cross-linked chelating resin is prepared and used which is faster, safer and prepared in more environmental friendly techniques for hardness removal, toxic, heavy metal ions removal, spillage clean up, metal ions pre-concentration for instrumental analytical purpose [9, 10]. In this paper, experimental studies of the performance of an in-house developed chelate group containing resin (polyacrylamide carboxylic acid PAC resin) by varying different process parameters viz., concentration, time, loading, mesh size, elution etc. have been stated.

Resin Properties

Functional group : Carboxylic acid
 Particle size range : 0.3 to 1.2 mm
 Operating pH range : 0 to 14
 Resistance to chemicals : Good
 Moisture holding capacity : 48–54%
 Rising space : 75% of bed depth [11]

EXPERIMENTAL

Materials and Equipment's Used

Chemicals such as calcium carbonate, hydrochloric acid, sulfuric acid, tartaric acid,

citric acid, nitric acid have been used without purification. In house prepared dry chelate resin is used during experiment. Filtrate and elute are analyzed by titration and AAS methods.

Acids: Hydrochloric acid, Sulfuric acid, Nitric acid, Tartaric acid, Citric acid of desired concentrations are prepared and acidities are checked by pH meter.

Calcium carbonate of required quantity is weighed and diluted in double distilled water up to desired concentration. Sorbent is dried at $100^\circ C$ in a hot air oven to remove residual water, then crushed, sieved and weighed according to the amount required.

Procedure

A certain amount of resin is weighed and contacted with the feed solution of certain concentration for a definite time period. After that, it is filtered. Loaded sorbent is retained on the filter paper and filtrate is taken into sample bottle. Feed and filtrate are analyzed with AAS.

Parameter Studied

Uptake

Uptake of calcium ion by the sorbent is calculated by carrying out mass balance of the calcium: $Q = [(C_1 - C_2) \times V]/m$

Percent Absorption

Percentage absorption of calcium by the sorbent is calculated as:

$$\% \text{ absorption} = [(C_1 - C_2) / C_1] \times 100$$

Extraction Procedure

The metal ion loaded sorbent was placed in the elution medium of certain volume and stirred for 3 h at room temperature.

$$\text{Elution ratio} = \frac{\text{Amount of metal ion eluted to the elution medium}}{\text{Amount of metal ions sorbed onto the elution medium}} \times 100$$

where, C_1 = initial concentration of the metal ion solution; C_2 = equilibrium conc.; V = volume of the feed solution; m = mass of the adsorbent; Q = uptake (mg/g of sorbent).

RESULTS AND DISCUSSION

Effect of Concentration Variation

Effect of concentration is found by loading 1 gm. of resin with varying concentrations of calcium from 100 ml. of calcium feed solution. The batch set-ups of the resin dipped into the solutions are kept overnight for equilibration and then filtered. Filtrates are analyzed by AAS [9]. Figure 2 shows the effect of calcium ion sorption with respect to variation of calcium ion concentration in feed solution. Percent sorption shows a steep increase up to 99.6% and then plateaus off. A marginal variation in the percent sorption from 99.6 to 99.8% w.r.t. the concentration of the influent 50 to 194 ppm respectively indicates substantial calcium uptake by the sorbent and the equilibrated value at the end of this curve is well above 99.5% which has been taken for the further parametric studies

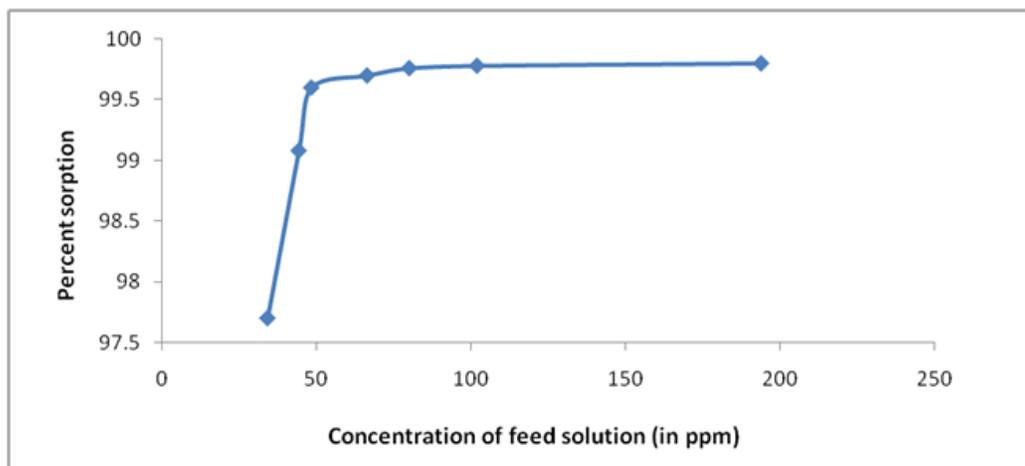


Fig. 2: Effect of Sorption by Resin with Concentration Variation.

Effect of Time Variation

Time variation study conducted with confirmed equilibrated value of calcium (which is approximately 200 ppm) containing feed solution for 5 min[12], 10 min[13], 15 min[14], 1 h[15], 2 h[16], 4 h[17], 8 h[18] time interval respectively by loading 1 g sorbent in 100 mL feed solution.

Immediately after the above mentioned time, solutions were filtered to separate loaded sorbent, filtrate. (Samples were analyzed by AAS. 1, 2, 3, 4, 5, 6, 7 in abscissa; denotes 5 min, 10 min, 15 min, 30 min, 1 h, 2 h, 4 h, respectively).

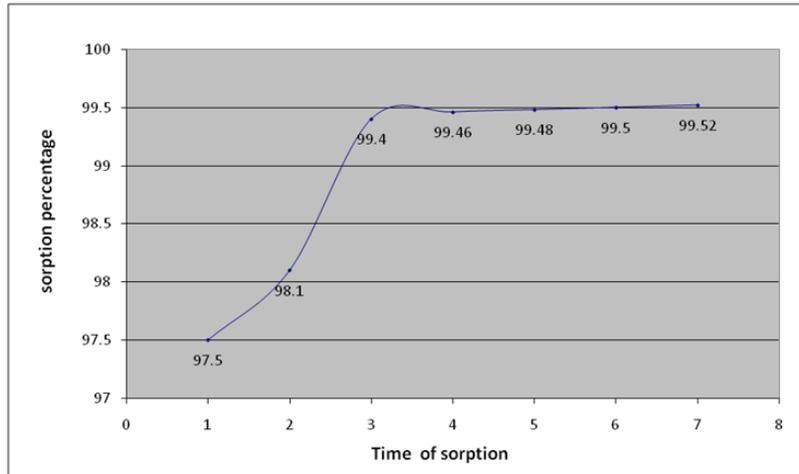


Fig.3: Effect of Sorption by Resin with Full Scale Time Variation.

In Figure 3, absorption percentage with respect to time interval shows an optimized value of 99.4% within 15 min. Although, beyond 15 min sorption percentage increases but after this time period; sorption percentage had not increased so substantially. Therefore, 15 min time was considered as sufficient time for desired sorption.

Effect of Mesh Size Variation

The dried resin is sieved through 10 ASTM,

16 ASTM, 18 ASTM, 20 ASTM and 30 ASTM mesh size sieve to obtain a definite fraction of sorbent for the study of mesh size variation. 0.5 g of each mesh size for 50 ml in 194 ppm feed solution was kept separately for 1 day equilibration, then filtered and analyzed. The bar diagram of this Figure 4 indicates calcium removal with respect to 10 ASTM, 16 ASTM, 18 ASTM, 20ASTM, 30ASTM mesh sized sorbent that sorbed 95, 98.68, 98.72, 98.9 and 99.2%, respectively.

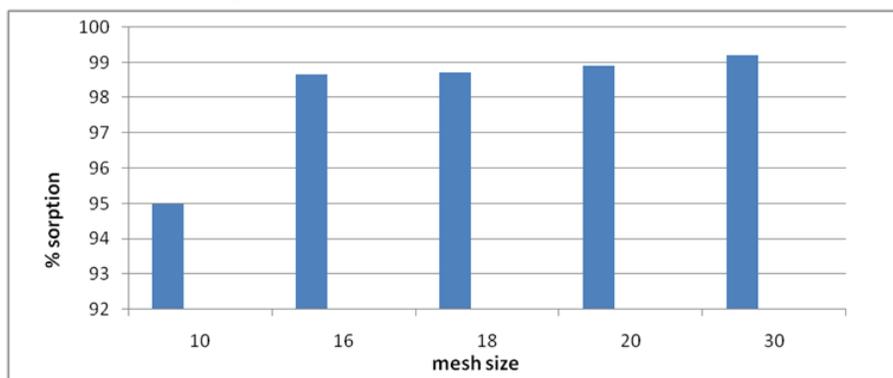


Fig.4: Percent Sorption in Mesh Size Variation.

In this regard, Figure 4 showed that resin in between 18 and 20 ASTM mesh size is more effective for desired purpose.

Effect of Dose Rate Variation

Loading of sorbent plays an important role to optimize the safe disposal of desired

outlet concentration. A 100 ml calcium containing solution of 194 ppm was contacted with 0.25, 0.5, 0.75, 1, 1.5 and 2 g of sorbent in separate conical flask and equilibrated for 24 h and then filtered. Filtrate was collected in sample bottles and analyzed. Figure 5 illustrates the effect of

dose rate variation/loading of sorbent with respect to calcium. Initially, with increased amount of sorbent, calcium sorption percentage also increases. Hence, it can be observed that 1 g resin for 100 mL solution was enough to reach the equilibrium for sorption of calcium.

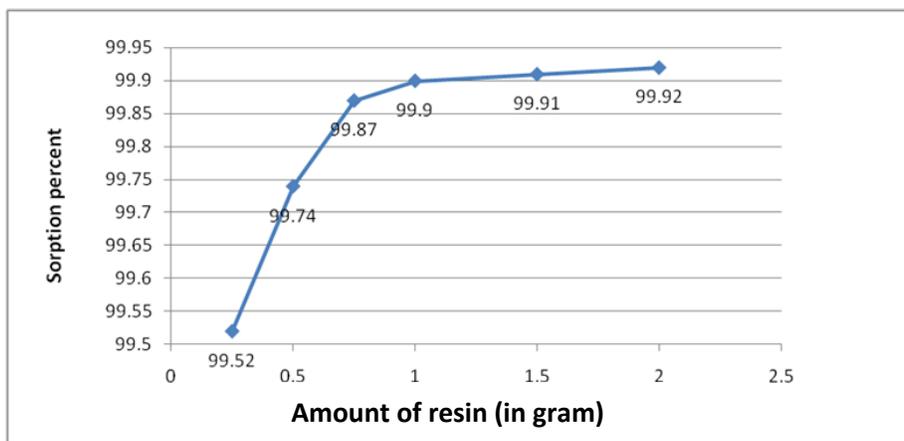


Fig.5: Percent Sorption in Dose Rate Variation.

Elution

In this study, 2N, 1N, pH-1, pH-2, pH-3 HCl solutions are contacted with loaded sorbent separately, and 98.8, 98.7, 96, 94.1 and 93.7% calcium removal are found in the elute. From the study, a comparison bar

diagram (Figure 6) is drawn and 1N hydrochloric acid solution has been selected. As for 2N hydrochloric acid solution degradation of the matrix is more. 1N hydrochloric acid is considered for further elution.

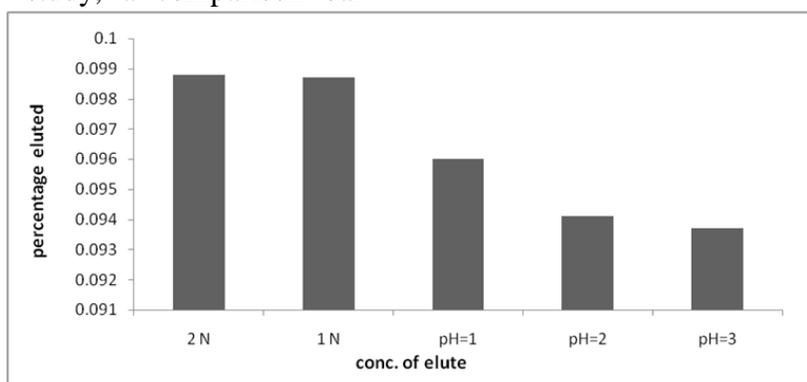


Fig. 6: Calcium Elution with Variation in Acidity.

CONCLUSION

Carboxylic acid has been developed in-house in Desalination Division, which is

capable of removing calcium to the extent of 98.5% in substantially short span of time of 5 min from feed containing calcium as high as 500 ppm and the resin work excellently

for streams having pH 4–7. Also, the loaded metal ions can be recovered and resin can be reused. In this regard, experimental studies by varying different process parameters viz., concentration, time, loading, mesh size, elution etc. have been reported in this paper to highlight the basic parameters for resin selection.

The study indicates experimentation with basic parameters like variation of concentration, time, mesh size, dose rate and elution for removal of calcium as a case study for hardness removal. The parametric studies for sorption of calcium ion by dry sorbent investigated in batch operation which exhibits substantial sorption (more than 99 %). within 15 min (99.4%) in contact with 18 to 20 ASTM mesh size sorbent having resin loading of 1 g/100 mL effluent. Elution with 1N HCl solution is most suitable (more than 98% elution) which helps in reuse of the sorbent. The above result indicates possibility to use the resin for removal of hardness or polishing of such type of hardness producing metal ions.

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