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EXTRACTION OF SOME CALCIUM AND MAGNESIUM SALTS FROM WASTE WATER OF REGENERATION PROCESS IN DEMINERALIZATION PLANT.

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ABSTRACT

The produced water from cation exchanger regeneration processes has been enriched by calcium and magnesium salts (very hard water). In this research, extraction of calcium and magnesium salts in the form of magnesium and calcium hydroxide (Lime) will carry out during adjusting pH of cation regeneration wastewater by adding anion regeneration wastewater. The extracted salts were dried and characterized by using chemical analysis, IR spectrum and X-ray analysis. Results indicated that an increase in the addition of anionic wastewater to cationic wastewater up to 60% caused a decrease in total hardness, magnesium hardness and calcium hardness concentrations in cationic wastewater up to 80%. However, the maximum percentage recovery of calcium salts obtained at pH values between 10-11, while those of magnesium salts were between 11-12.

Keywords: Waste water, Hardness, Cation exchanger, Calcium, Magnesium, Regeneration.

INTRODUCTION

Demineralization water treatment or de ionization water treatment process is the removal of essentially all inorganic salts by ion exchange. In this water treatment process, strong acid cation resin in the hydrogen form converts dissolved salts into their corresponding acids, and strong base anion resin in the hydroxide form removes these acids^[1]. Demineralization water treatment plant produces water similar in quality to distillation at a lower cost for most fresh waters. A demineralizer water treatment system consists of one or more ion exchange resin columns, which include a strong acid cation unit and a strong base anion unit^[2]. The wastewater produced from regeneration process has a higher amount of salts especially calcium and magnesium salts^[3]. This wastewater is like brine solution (saline solution). Previous studies have shown that salts in brine can be recovered and purified as commercial products. Salts have been recovered from salty lakes^[4], sea water^[5], textile effluent^[6], concentrate at a sugar decolorization plant^[7], and industrial effluent^[8,9].

Due to the lack of adequate methods for the disposal of waste brine produced during demineralization processes, environmental pollution will be created. The most common methods to treat concentrates include: (1) disposal to evaporation ponds^[10-12], (2) discharge in deep disused gold mines or wells^[13] and (3) coastal discharge^[14].

^[6]. However, Buckley, et al. (1987)^[17] suggested the following additional methods for treatment of waste brine:

(1) Engineering out the source of brine: reducing the dissolved solids in the brine by implementing chemical or engineering changes in the production process.

(2) Converting brine into useful chemicals: recycling, or recovering chemicals or salts from the waste brine.

(3) Deactivation or conversion of brine to an inert substance: deactivating waste brine by transforming it into unreactive or insoluble compounds.

The objective of this work is to find a new technique to extract some salts from cation exchange waste water by the addition of anion exchange waste water at proper conditions.

METHODS AND MATERIALS

Source of Water Works Samples:

2-1-1. Very hard wastewater was obtained from Cation Regeneration Waste Water (CRWW) of demineralization plant with an ingredients present in table (1).

2-1-2. Alkaline wastewater was obtained from Anion Regeneration Waste Water (ARWW) of the same demineralization plant with an ingredients present in table (1).

2-2. Precipitation of Calcium and Magnesium salts:

A calculated amount of (ARWW) was added to one liter of (CRWW). The pH of (CRWW) was increased by these additions until reached to 10.5 at this point calcium carbonate was precipitated and isolated by filtration through filter paper. The remained filtrate will go through furthermore addition of (ARWW). This addition leads to increase pH to 11.5 at this point magnesium hydroxide precipitated and isolated by filtration. Both of two precipitates were heated at 650C⁰ to produce calcium and magnesium oxide.

2-3. Chemicals Analysis and Tests:

2-3-1. Chemicals:

- Calcium and magnesium oxide of pure grade used as standard materials.

- All chemicals that used in the analysis in this work were of laboratory chemical grade.

2-3-2. Analysis:

The following series of water examination and chemical analysis were carried out accord-

ing to the standard method of ASTM Book of Standards (ASTM, 2001).

- Total hardness, Calcium and magnesium hardness and alkalinity of water determined in (mg/L) as CaCO₃ by titration with EDTA according to ASTM Book of Standards (ASTM, 2001).

- pH of waste water was measured by pH meter model 810 Fisher scientific .

- The removal efficiency (% Recovery) was calculated from the following formula:

$$\% Recovery = C_0 - C / C_0 \times 100$$

Where, C₀ and C = initial and final concentration of the elements.

- X-ray analysis of dry salts: The dry salts of calcium and magnesium were analyzed by using; Energy Dispersive X-ray System., ISIS Link Instrument P/C. Oxford Co.

- IR spectra were performed by using FTIR-ATR spectra of the above mentioned samples were recorded by means of Nicolet 380 Spectrometer. The FTIR absorbance frequencies for the samples were recorded with an average of 128 scans using a resolution of 4 cm⁻¹.

Table (1) Chemical analysis of Cation and Anion Waste Water .

Cation waste water		Anion waste water	
Analysis	value	Analysis	value
Ph	6.61	pH	12.75
Total Hardness mg/L(as CaCO ₃)	3000	Total alkalinity mg/L(as CaCO ₃)	11300
Calcium Hardness mg/L (as CaCO ₃)	1750	Sodium mg/L as Na	6875
Magnesium Hardness mg/L (as CaCO ₃)	1250	Sulphate mg/L as SO ₄ ⁻	1850
Sodium mg/L as Na	870	Chloride mg/L as Cl ⁻	6300
Iron mg/L as Fe	2.9		

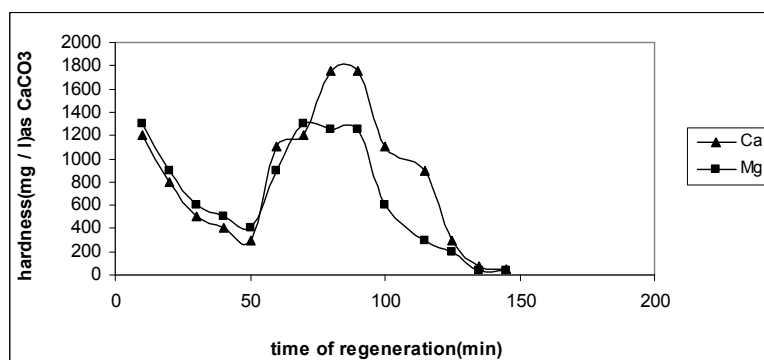


Figure (1): Variation of Calcium and Magnesium hardness during regeneration time of exhausted cation exchange.

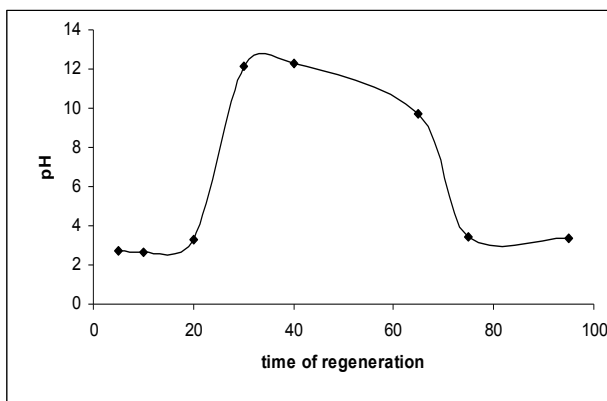


Figure (2): Variation of pH value during regeneration time of exhausted anion exchange.

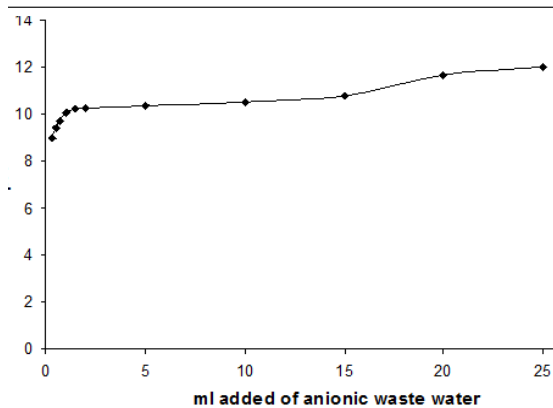


Figure (3) Effect of ml added of (ARWW) on the pH of (CRWW).

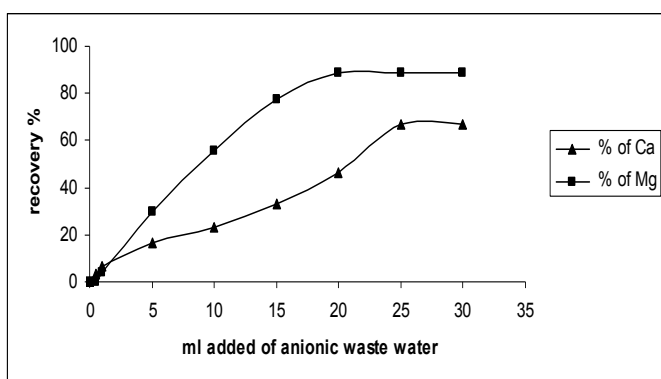


Figure (4) Effect of ml added of (ARWW) on % recovery of calcium and magnesium ions.

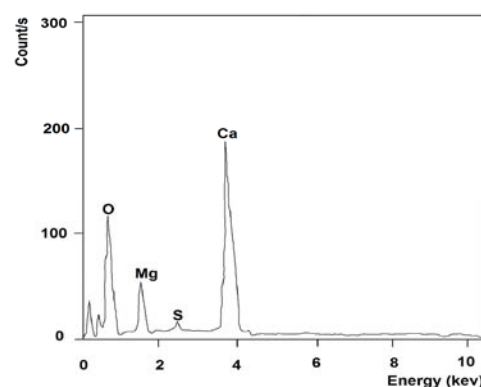


Figure (5) X-ray of extracted salt at pH 10.5.

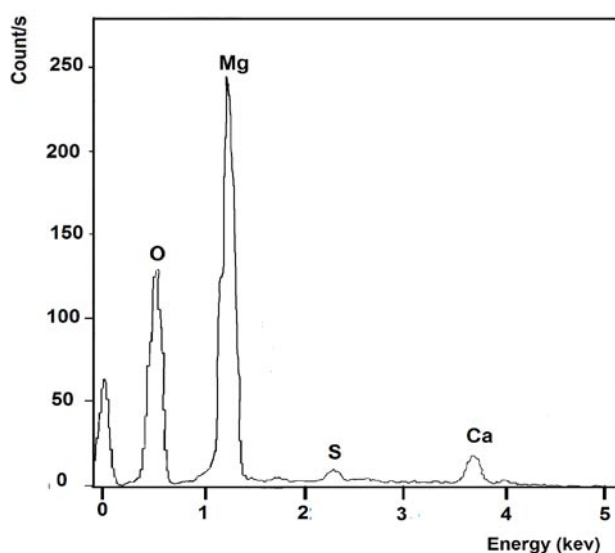


Figure (6) X-ray of extracted salt at pH 11.5.

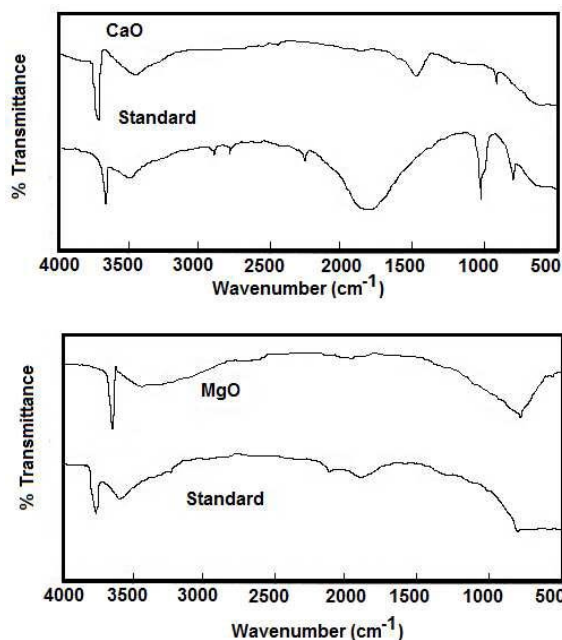


Figure (7) FTIR Spectra of recovered and standard calcium and magnesium oxide.

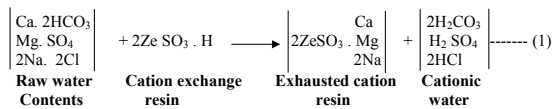
RESULTS AND DISCUSSION

3-1. Theory of Ion Exchange in the Demineralization Plants

The process of water demineralization is operated in the demineralization plant as follow:

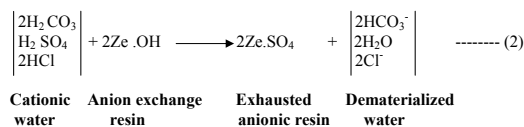
3-1-1. Operation Process of Cation Exchange:

The most ingredients of working raw water are Calcium and magnesium salts present in the form of (sulphates, chlorides, carbonates and bicarbonates). When this water passed through cation exchange resin, the exchange occurs according to equation (1):



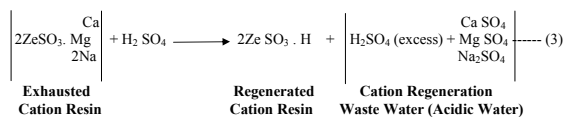
3-1-2. Operation Process of Anionic Exchange:

The cationic water passed through anion exchange resin, the exchanges are donning to produce demineralized water according to equation (2):



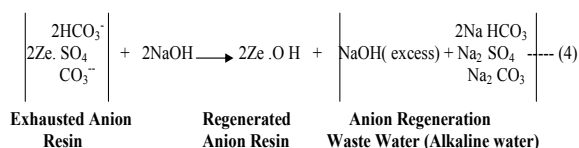
3-1-3. Regeneration Process of Cation Exchange:

After ion exchange resin exhaustion the resin will go through regeneration processes. The regeneration process occurs by using sulfuric acid according to equation (3):



3-1-4. Regeneration Process of Anion Exchange:

The regeneration process occurs by using sodium hydroxide according to equation (4):



3-2. Characterization of Waste Water:

From the above mentioned processes we have two kinds of waste water; Cation Regeneration Waste Water (CRWW) collected from demineralization plant during regeneration process of cation exchange resin and Anion Regeneration waste Water (ARWW) collected from demineralization plant during regeneration process of anion exchange resin. The chemical analysis of (CRWW) revealed that it has been enriched by calcium and magnesium salts as can be seen from table (1). During the regeneration process calcium and magnesium hardness was at maximum concentration after 80 minutes from the beginning of regeneration process of cation exchange resin as can be seen from figure (1). While the maximum pH of (ARWW) where found after (30-40) minutes from the beginning of regeneration process of anion resin at this point the (ARWW) was enriched by mixture of sodium (Hydroxide, sulphate, carbonate and bicarbonate) as can be seen from figure (2). Table (1) show the chemical analysis of (CRWW and ARWW). The samples were withdrawal at the maximum concentration of calcium and magnesium for (CRWW), while at maximum pH for (ARWW).

3-3. Calcium and Magnesium Recovery and Determination:

3-3-1. Hardness Removal Process:

Water utilities struggling with source water that contains high amounts of calcium and/or magnesium often turn to lime softening to remove hardness. Raising treatment pH above 9.6 converts soluble calcium bicarbonate hardness to insoluble calcium carbonate. An increase in pH beyond 10.6 converts soluble magnesium bicarbonate to insoluble magnesium hydroxide. Aggressive magnesium removal often requires a treatment pH range 11-12.

During precipitation softening, calcium is removed from water in the form of CaCO_3 precipitate and magnesium is removed as Mg(OH)_2 precipitate. The pH plays an important role in the precipitation of these two solids. Carbonate hardness can be removed by the addition of hydroxide ions and raising the pH by which the

bicarbonate ions are converted to carbonate form having a pH above 10. Due to the increase in carbonate concentration, precipitates of calcium carbonate are formed. The remaining calcium, i.e. non carbonate hardness, cannot be removed by simple adjustment of pH. Therefore, soda ash (sodium carbonate) must be externally added to precipitate this remaining calcium. Magnesium is removed due to the precipitation of magnesium hydroxide. In the lime soda ash process, lime is added to raise the pH while sodium carbonate is added to provide a source of carbonate ion.

3-3-2. Precepitation of Calcium and Magnesiumsalts:

The anion regeneration waste water (ARWW) which contains sodium (carbonate, bicarbonate and hydroxide) can provide an excellent condition for precipitation of calcium and magnesium salts when added to cation regeneration waste water (CRWW).

Therefore the addition of (ARWW) to (CRWW) were studied in accordance to provide maximum precipitation level expressed as percentage recovery by ml added. Figure (3) show the precipitation profile of calcium and magnesium salts during the addition of (ARWW) to the (CRWW) expressed as % recovery by ml added. The results indicate that the maximum % recovery of calcium was found by adding 20 ml, while for magnesium by adding 25 ml of (ARWW) to 100 ml of (CRWW). Also the results indicate that the (pH) increase with increasing (ml) added of (ARWW) as can be seen from figure (4). Furthermore the increasing of (pH) leads to increase the precipitation level of calcium and magnesium salts.

Figure (4) show that the maximum % recovery of calcium salts obtained at (pH) value between 10-11, while magnesium salts was between 11-12. Nevertheless the percentage recovery reached to 66.66% and 88.88 % for calcium and magnesium salts respectively as can be seen from figure (4).

3-3-3. Nature of the Extracted Salts:

The extracted calcium and magnesium salts were introduced to investigation as follow:

3-3-3-1. X-ray analysis of extracted salts:

The extracted salts at pH (10.5) and (11.5) were analyzed by using; Energy Dispersive X-ray System. The results are shown in figures (5, 6). It is clearly seen that for salt extracted at pH (10.5) the main peak in the chart was for calcium. Also for the salt extracted at pH (11.5) the main peak was for magnesium.

3-3-3-2. IR SPECTROSCOPY:

The nature of the produced salts was performed by IR spectra using FTIR-ATR spectra of the above mentioned samples. Figure (7) represent the IR spectra of both the standards CaO and MgO samples in comparison with extracted products from the waste water. The curves show that there is agreement between peaks of the extracted CaO and MgO with the standard samples.

CONCLUSION

Extraction of calcium and magnesium salts in the form of magnesium and calcium hydroxide (Lime) will carry out during adjusting pH of cation regeneration waste water by adding anion regeneration waste water. Results indicated that an increase in the addition of anionic waste water to cationic waste water up to 60% caused a decrease in total hardness, magnesium hardness and calcium hardness concentrations in cationic waste water up to 80%. However, the maximum percentage recovery of calcium salts obtained at pH value between 10-11, while magnesium salts was between 11-12.

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