



REDUCTION OF SO_4^{2-} AND Cl^- IONS FROM INDUSTRIAL WASTE WATER BY ION EXCHANGE

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ABSTRACT

This work was conducted to study the removal of ionic impurities from industrial wastewater, and more particularly those in the cotton textile industry. The wastewater considered here, contains both cation and anion impurities. The method used is ion exchange. The results showed that the equilibrium isotherm is strongly favorable type, and it fitted well with Langmuir equation. Chlorine and Sulphate ions were reduced greatly but not with the same degree ($SO_4^{2-} > Cl^-$).

الخلاصة

تضمن هذا البحث دراسة إزالة الملوثات الايونية من المياه الصناعية، و خاصة مصانع الأنسجة القطنية. حيث تحتوي هذه المياه على ملوثات ايونية موجبة و سالبة الشحنة. تم استخدام المبادلات الايونية لإزالة تلك الملوثات. و من خلال منحنيات التوازن دلت النتائج على ان هذه العملية ملائمة جدا و ان تلك المنحنيات متطابقة مع معادلة لانكيمير، كما لوحظ ان أيونات الكبريتات تتناقص أسرع من أيونات الكلوريدات.

KEY WORDS

Removal of anions, Ion exchange, Waste water treatment

INTRODUCTION

Ion exchange is used extensively for water and wastewater treatment, primarily for the removal of "hardness" ions (Ca^{2+} and Mg^{2+}) from water supplies, and for the removal of iron and manganese from ground water supplies. It has also been used selectively to remove specific impurities, and to recover valuable trace metals like chromium, copper, lead, cadmium, and nickel from industrial waste discharges. The process takes advantage of the ability of certain natural and synthetic materials to exchange one of their ions with another contained in the water passing through them (Mulligan, 1976). In the process contaminated water is passed through a packed bed of anion and or cation resin. The resin type is selected based on the contaminant to be removed (California WPUB, 2001).

For many industrial purposes, such as high-pressure boiler systems, critical-materials heat transfer systems, certain rinsing operations, and electronics and pharmaceuticals processing applications, waters of very low total dissolved solids concentrations are required. Ion exchange is a particularly suitable water treatment process for such applications (Degremont, 1979).

The principles of water demineralization and water softening by ion exchange are essentially the same. The differences are that both cation and anion exchangers are used for demineralization, and the exchange resins are utilized in the hydrogen and hydroxide forms, respectively. By using

hydrogen and hydroxide form exchangers, the exchangeable ions released to solution as the exchange operation proceeds are simply hydrogen and hydroxide ions, which (unlike sodium and chloride ions, for example) contribute nothing to the dissolved solids concentration of the treated water (Kunin, 1958).

Demineralization of wastewater is achieved in two steps (the cation and anion exchange steps). The positive ions such as *Ca*, *Mg* or *Na* are removed in the cation exchanger using a hydrogen cycle.

The general principles of ion exchange operation may be logically extended to specific industrial waste-treatment operations in which it is desired to remove ionic impurities. Treatment of wastes by ion exchange is somewhat complicated of course by the presence of materials or conditions, which may clog, attack, or foul resins. Serious chemical or thermal attack of modern synthetic resin is unusual.

Polystyrene-divinyl benzene resins are very resistant to chemical and physical attrition and are insoluble in all common organic and inorganic solvents, including mineral acids and bases. High concentrations of oxidizing agents such as nitric acid have deteriorious effects by attacking the resins at vulnerable cross links. Regarding temperature stability, most resins are stable to 100°C or higher (Kunin, 1958).

As noted earlier one important application of ion exchange in waste treatment is for recovery of valuable metals from industrial waste streams. A major example is the recovery of hexavalent chromium (Cr^{6+}) from plating wastes, with subsequent reuse of the treated water (Keating, 1954).

Resins used for plating waste applications generally have greater regeneration requirements than cation resins employed for removal of Ca^{2+} and Mg^{2+} in water softening applications because of competition with H_3O^+ ions in the acidic plating wastes (Weber and Walter, 1972).

EXPERIMENTAL

Analysis

The electrical conductivity of the industrial wastewater and the concentration of general ions must first be measured. Then a model solution is prepared taking the maximum concentration of Cl^- and SO_4^{2-} ions, which represent the general problem of treatment, where the ratio of Cl^- ions to SO_4^{2-} ions is 5 : 7 in the wastewater. 0.25 gm of *NaCl* as Cl^- ion was mixed with 0.35 gm of *MgSO₄* as SO_4^{2-} ion in 1 liter of distilled water, the conductivity of the solution was measured (795 $\mu s/m^3$) and the total salt content was equal to 600 ppm.

Exchange Isotherm Determination

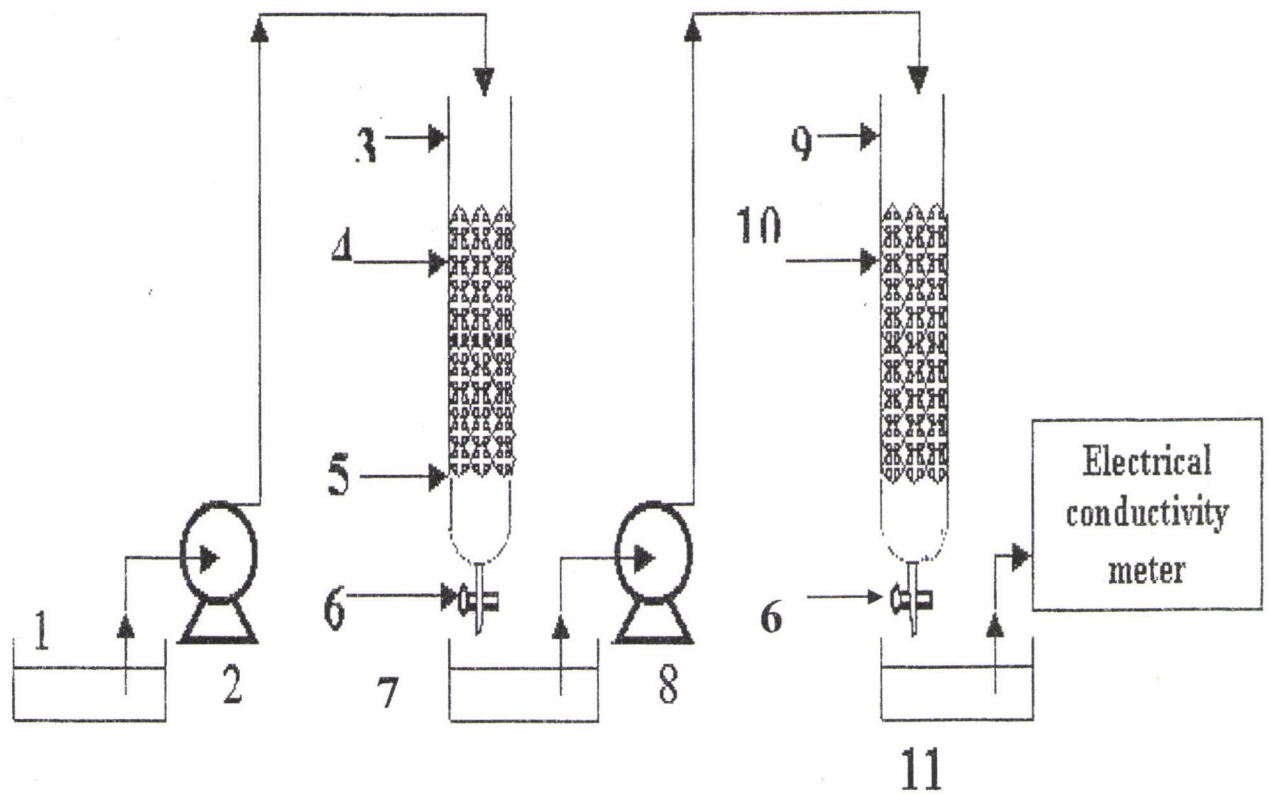
The procedure used is that the standard salt solution content was chosen to be greater than the maximum concentration considered (for example 700 ppm) and its conductivity (930 $\mu s/cm$). A measured volume of this salt solution was added to different weights of resins (cation and anion resins in equal ratio) in a flask. These samples were put in a constant temperature shaker and after equilibrium was reached, the liquid was analyzed using electrical conductivity meter. The experiments were carried out at a temperature of 27°C.

The exchange isotherm was obtained by plotting the weight of the salt exchanged per unit weight of resin against the equilibrium conductivity of the solution.

Experimental Procedure

The exchange abilities of cation-anion resins under dynamic conditions for model salt solution were investigated using glass columns with diameter of 1.27 cm and a length of 50 cm and co-current flow. The cation column contained 20.88 gm of resin, while the anion column contained 10.35 gm of resin, having the same bed height. The resin size ranged from 0.8 to 1.2 mm.

The model salt solution ($C_0 = 600$ p.p.m.) was introduced at the top of the column of the cation resin using a dosing pump at a constant volumetric flow rate of 1 L/h. Then another dosing pump was used to pump the solution to the column of the anion resin. Samples were taken every 10 minutes, and the conductivity of these samples were measured using electrical conductivity meter. Fig. (1) shows a schematic diagram of the experimental rig.



- | | |
|-----|--|
| 1 | Salt solution reservoir |
| 2,8 | Dosing pump |
| 3,9 | Glass column (12.7 mm diameter, 500 mm long) |
| 4 | Cation resin |
| 5 | Sieve of fine porosity |
| 6 | Controlling valve |
| 7 | Partially treated solution |
| 10 | Anion resin |
| 11 | Final treated solution |

Fig. (1) Ion exchange system

The pH of the solution leaving the cation column was measured during the process. If the pH of the solution was more than 6 (Brands and Tripke, 1982) then the resin required regeneration. First the resin was backwashed with distilled water then regeneration of the resin was carried out using

hydrochloric acid solution of 4 wt% concentration. The time of regeneration was about 30 minutes. After that, the column of the cation resin was washed with distilled water and reused.

The pH of the solution leaving the anion column was measured during the process. If the pH of the solution was less than 8, the resin required regeneration. The resin was backwashed with distilled water, then regeneration of the resin was carried out using sodium hydroxide solution of 4 wt% concentration. Regeneration time was about 30-45 minutes. Then the column of anion resin was washed with distilled water and reused. Breakthrough curve was determined by plotting effluent conductivity from the cation-anion unit against time. A calibration curve for concentration vs. conductivity was made using known standard salt concentrations that were prepared by mixing the same ratio of NaCl to MgSO_4 salts in distilled water then finding their conductivity.

DISCUSSION

Ion Exchange Isotherm

Because ion exchange is one form of sorption from solution (exchange sorption) it is usually feasible to describe the equilibrium distribution of an ion phase in terms of one of the conventional adsorption isotherm expressions. **Fig.(2)** shows the isotherm curve for the experimental system used. This curve is drawn as the change in the conductivity of the salt solution against the conductivity of the salt solution, at a constant temperature (27°C). For the design requirement, the conductivity values must be converted to salt concentration. For this purpose a standard solutions were prepared and a calibration curve was plotted and fitted. The

data show the same isotherm behavior. Moreover, these isotherms are fitted well with Langmuir equation ($q_e = \frac{abC}{1 + bC}$). The Langmuir equation constants and correlation coefficients are tabulated in **Table (1)**.

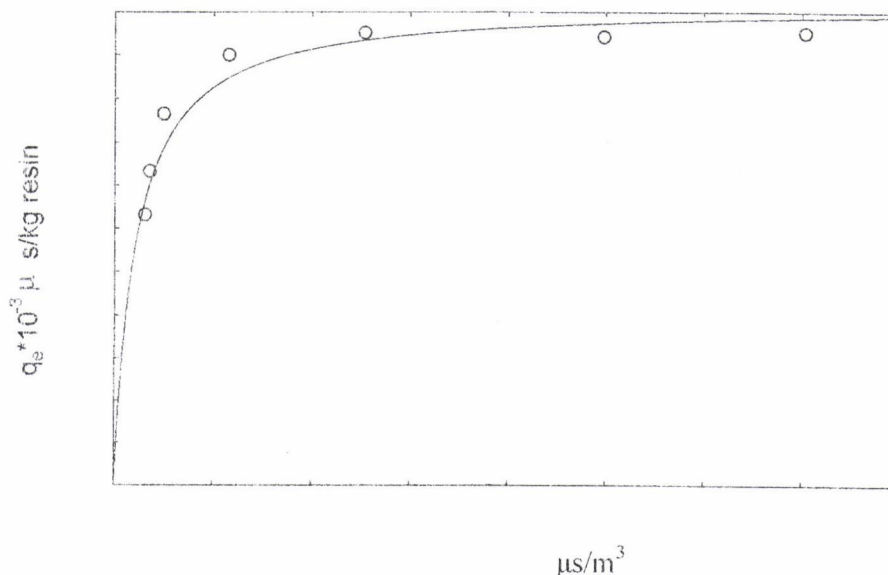


Fig.(2) Ion exchange isotherm curve at 27°C

Table (1) Langmuir equation constants for the ion-exchange

	a	b	Correlation coefficient
Conductivity	111.84 $\mu\text{s}/\text{kg resin}$	0.048 $\text{m}^3/\mu\text{s}$	0.967
Concentration	90.99 $\text{kg salt}/\text{kg resin}$	0.03 $\text{m}^3/\text{kg salt}$	0.944

The equilibrium isotherm is convex upward, because a relatively high resin loading were obtained at low concentration of salt in the water. This isotherm is of strongly favorable type. Commonly, the amount of adsorbed salt per unit weight of resin increases with increasing concentration but not in direct proportion.

Ion Exchange Breakthrough Curve

Fig. (3) shows the experimental breakthrough curve for ion exchange of salt solution through cation-anion resins, based on the change in conductivity of the solution with time. And, the change in salt concentration with time is shown in **Fig.(4)**. It can be noted that the breakthrough curve had a sharp form, may be due to the rapid saturation of the resin during the operation process.

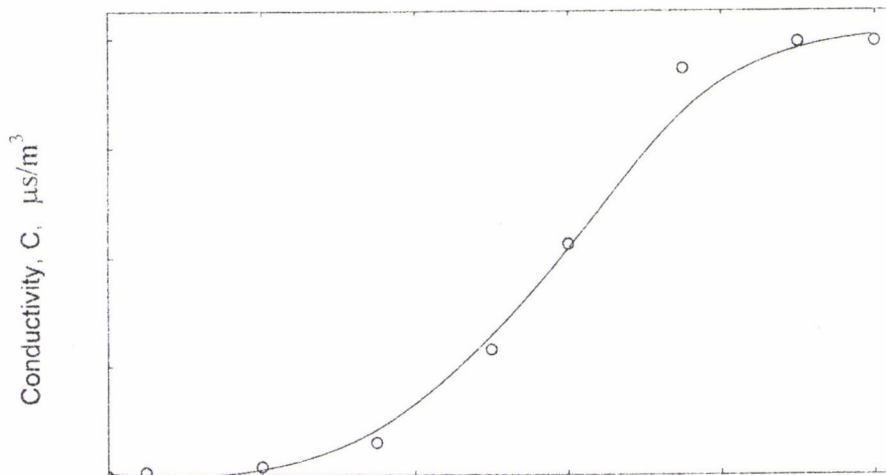


Fig.(3) The experimental breakthrough curve for ion exchange of salt solution through cation-anion resins

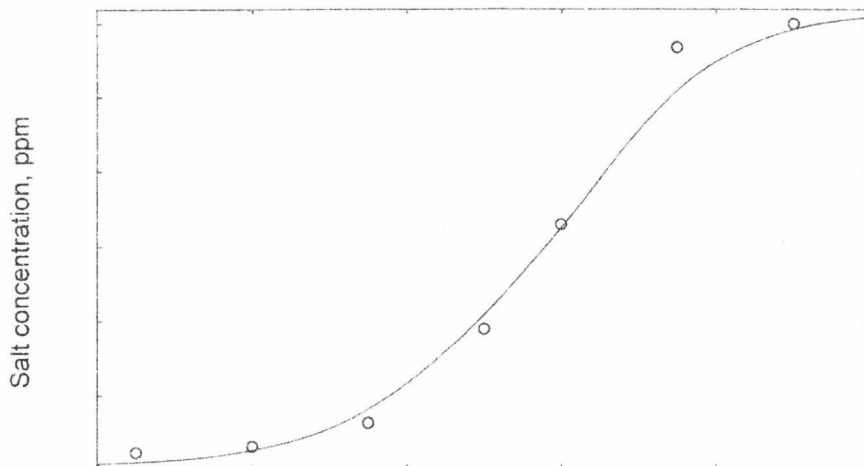


Fig.(4) The concentration breakthrough curve for salt solution with ($C_o = 600$ ppm)

Chlorine and sulphate ions decreased due to the action of anion resins but not at the same degree ($SO_4^{2-} > Cl^-$). This could be due to that ions of higher charge are preferentially exchanged. Also the sodium and magnesium ions (and calcium, if present) decreased due to the action of cation resins so that the total hardness and alkalinity are reduced.

However for the particular case of this study, viz. the treatment and recycling of industrial wastewater from cotton – textile industry and to reduce the cost of treatment, anion exchange unit only can be used instead of cation-anion exchange unit, because the Mg^{2+} , Ca^{2+} ions in the treated solution and in the raw water fed to the factory were not very much different, on the contrary the Cl^- , SO_4^{2-} ions has a higher concentration than in the raw water fed to the factory, so that it only required anion exchange unit for reducing their concentration.

CONCLUSIONS

- 1- Ion exchange equilibrium isotherm is convex upward, because a relatively high resin loading were obtained at low concentration of salt in the water. This isotherm is of strongly favorable type.
- 2- The equilibrium isotherms are fitted well with Langmuir equation.
- 3- Ion exchange breakthrough curve had a sharp form, due to the rapid saturation of the resin during the operation process.
- 4- Chlorine and sulphate ions were reduced but not with the same degree ($SO_4^{2-} > Cl^-$).
- 5- For cotton – textile industrial wastewater treatment and recycling unit, the anion exchange column may be used instead of cation – anion columns to reduce the cost of treating.

NOMENCLATURE

a : Langmuir “monolayer” capacity , conductivity	$\mu\text{s}/\text{kg resin}$
, concentration	$\text{kg salt}/\text{kg resin}$
b : Langmuir equation constant at constant temperature , conductivity	$\text{m}^3/\mu\text{s}$
, concentration	$\text{m}^3/\text{kg salt}$
C : Conductivity for ion exchange	$\mu\text{s}/\text{m}^3$



Or, solute concentration in solution kg salt/m^3
 q_e : Amount of solute adsorbed per unit mass of solid adsorbent, conductivity $\mu\text{s/kg resin}$
, concentration kg salt/kg resin

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