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Reactive Polymers in Mercury Removal from Electrolytic Brine

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Abstract: The adsorption of mercury from concentrated aqueous solutions and chlor-alkali industry brine on the reactive polymers has been studied. The investigations were performed in the batch and column systems. The batch experiments were carried out to assess mercury ion exchange adsorption isotherms and adsorptive capacity. The effects of agitation time and pH were investigated. On the basis of dynamic experiment results, mercury concentration in the effluent obtained from the column against the flow rate of brine through the bed was deduced and the effective and total capacities were calculated. The regeneration of the spent resins was also investigated.

Keywords: Electrolytic brine, mercury, reactive polymers, removal

INTRODUCTION

Mercury is one of the most hazardous contaminants in the natural environment inasmuch as it spreads easily and accumulates in living organisms. It is found (max. 10 mg/l) in the wastewaters coming from the chlor-alkali manufacturing industry. The maximum level of mercury authorized in Polish industrial effluents is 0.05 mg/l (wastewaters produced by mercury amalgam process). Because of this and due to the high toxicity of mercury compounds, in particular to the human nervous

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system, waste electrolytic brine should be treated by removing mercury prior to its further usage.

Various types of technology are available for removing mercury from water and wastewater, including chemical precipitation (1–3), conventional coagulation/co-precipitation/adsorption (2–5), membrane technique (6–8), activated carbon adsorption (9–12), and ion-exchange (13–18). Concentrated brine exhibits high ionic strength and thus its properties are different from those of diluted solutions which should be taken into consideration while selecting the treatment methods. There are not many researches on mercury removal from concentrated salty solutions (10% (w/w) and over).

The ion exchange technique is very efficient in removing trace amounts of mercury from the solutions of large volume and ion exchange systems are easy to develop. It is possible to remove Hg(II) ions from waters and industrial wastewaters on various types of ion exchangers e.g. strongly acidic cation exchangers, weakly and strongly basic anion exchangers, as well as on selective ion exchangers of various types (19–21). Unconventional ion exchange resins are also applied (22–24). The commonly used chelating ion-exchanger Dowex A-1 and its purified form Chelex 100 with functional iminodiacetate groups exhibit high selectivity for Hg(II) ions (25). The functional groups containing amino groups are also suitable for the selective removal of mercury(II) from its aqueous solutions (adsorption capacity of 1.06 mmol/g) (26).

Many industries apply the selective ion exchanger Imac TMR (Akzo Zout) to the selective removal of Hg(II) ions from technological solutions, primarily from electrolytic brines. Imac TMR is a styrenedivinylbenzene copolymer which has mainly functional thiol groups, a number of sulphonic groups and exhibits a macroporous structure. Its capacity for Hg(II) ions is 240 g Hg/l of ion exchanger. It is possible to diminish the mercury content in wastewaters down to 0.5–5.0 ppb, using the ion exchanger Imac TMR. After the Hg(II) ions sorption, the ion exchanger Imac TMR can be regenerated by means of concentrated hydrochloric acid solution (27).

Besides the ion exchanger Imac TMR discussed above, the following ion exchangers possess thiol groups: Duolite ES-465 (Dia-Prosim), Chelite S (Serva), Duolite GT-73 – renamed Amberlite GT 73 now – (Rohm and Haas), and Spheron Thiol (Lachema). At present, only Amberlite GT-73 is produced on a commercial scale (28). Its capacity is assessed at 1.2 eq/l.

Another group of ion exchangers exhibiting great selectivity for Hg(II) ions are those containing N and S functional groups—Varion BTAM (Nike), thiocarbamate group—Varion BTKM (Nike), mercapthile group-Varion BSM (Nike) and thiourea functional groups like Ionac SR-3, Ionac SRXL (Ionac), Lewatit TP-214 (Bayer -Lanxess), Monivex (Ayalon), Purolite S-920 (Purolite), Srafion NMRR (Ayalon, Serva), Sumichelate Q-10 (Sumitomo), Relite MAC-3 (Residion, USA).

Srafion NMRR is most commonly applied to Hg(II) removal from industrial wastewaters. Its sorption capacity for Hg(II) ion is 545 g Hg/kg of ion exchanger. 5% thiourea solution containing 0.22% HCl is used for the desorption of Hg(II) from its bed (29). The comparison of a selective ion exchanger was presented in the paper (30).

In this study, the removal of mercury from NaCl concentrated aqueous solutions and chlor-alkali industry brine on ion exchange resins under varying conditions of agitation time, metal ion concentration, pH, and temperature have been examined. The novelty of this paper is using concentrated salty solution (brine from chemical industry) in all experiments that is presented in available literature very poor.

EXPERIMENTAL

Reagents

A basic standard solution of mercury(II) in the form of mercury(II) nitrate(V) – 1 g Hg/l – prepared from 1 g metallic mercury (accuracy of 0.0001 g) and 100 ml concentrated nitric(V) acid in a 1-l measuring flask, durable for 1 year; working mercury(II) solution – 1 mg Hg/l – freshly prepared by diluting the basic solution; a basic standard mercury(II) solution in the form of mercury(II) chloride – 1 g Hg/l – prepared from a weighed portion of $HgCl_2$, analytical grade (accuracy of 0.0001 g) and 100 ml of concentrated hydrochloric acid in a 1-l measuring flask, durable for 1 year, sodium chloride, analytical grade – solution concentration of 25% (w/w); sodium hydroxide, analytical grade – solution concentration of 5 and 20%, hydrochloric acid, analytical grade – solution concentration of 1 mol/l, sodium hydrosulfonate(IV), analytical grade. All reagents were produced by POCh situated in Gliwice (Poland).

Ion Exchangers

The data concerning the ion exchangers used are given in Table 1.

Composition of Electrolytic Brine

$NaCl = 312.6$ g/l, $Ca^{2+} = 0.142$ g/l, $SO_4^{2-} = 9.805$ g/l, $Cl_2 = 0.035$ g/l, $Fe^{3+} = 3.95$ mg/l, $Al^{3+} = 0.140$ mg/l, $Hg^{2+} = 6$ mg/l, other ions < 1 mg/l, $pH = 3.7$, density $\rho = 1.198$ g/ml.

Table 1. Selected physical and chemical properties of mercury resins, WAC – weakly acidic cation exchange resin, WBA – weakly basic anion exchange resin, SBA – strongly basic anion exchange resin

Resin name	Resin type	Matrix type	Active center	Particle size [mm]	pH range	Reccomended flow rate BV/h	Total capacity [eq/l]	Manufacturer
Amberlite GT 73	WAC Hg Specific	polystyrene	Thiol (dithiol) $[R\text{-}(SH)_2]$)	0.45–0.70	1–13	16.2–62.4	≤1.2	Rohm & Haas
Amberlite IRA 410	SBA (type II)	polystyrene-divinylbenzene	Quaternary ammonium	20–50 mesh	0–14	10	1.4	Rohm & Haas
Lewatit MonoPlus TP 214	Hg Specific Chelating	polystyrene	Thiourea	0.55(± 0.05)	0–10	5–20 m/h	For Ag 2.0	Lanxess Energizing Chemistry
Lewatit TP 207	WAC	polystyrene	Iminodiacetic acid ($[R\text{-}N\text{-}(CH_2COO^-)_2]$)	0.4–1.25	1.5–9	Max. 40	2.2	Lanxess Energizing Chemistry
Lewatit MP 62	WBA	polystyrene	Tertiary amine	0.315–1.25	0–8	Max. 40	1.7	Lanxess Energizing Chemistry
Purolite S 930	WAC Chelating	polystyrene-divinylbenzene	Iminodiacetyldiacetic acid	0.425–1.2	H^+2–6 Na^+ 6–11	10–12	Min. 2.4	The Purolite Company
Purolite S 920	WAC Hg Specific Chelating	polystyrene-divinylbenzene	Isothiouronium ($[R\text{-}S{=}C\text{-}(NH_2)_2]$)	0.3–1.2	1–9	10	1.6	The Purolite Company
Purolite A 500	SBA (type I)	polystyrene-divinylbenzene	Quaternary ammonium (trimethylammonium ($[R\text{-}N\text{-}(CH_3)_3]^+$))	0.3–1.2	0–12	40	1.15	The Purolite Company

Apparatus and Laboratory Equipment

An atomic absorption spectrometer 3300 (Perkin Elmer) equipped with an MHS-10 attachment to generate hydrides and mercury vapour, a PC and software; a cathode mercury lamp (Photron Perkin Elmer, Australia); argon, purity 99.998%; HTL micropipettes (Dom Handlowy Nauki, Cracow); a WU universal shaker (PREMED, Warsaw); WPE 120 electronic balance ("Radwag", Radom); ion exchange columns, inside diameter of 8 mm; laboratory glassware and small equipment: conical flasks with ground glass joint, measuring flasks, beakers, chemical funnels.

Methods

Batch mode adsorption studies were carried out with 20 mg of ion exchange resin (shown in Table 1) and 50 ml of Hg(II) of a desired concentration in 25% NaCl solution at pH 3, 3.7, 7, or 11 in 250-ml conical flasks with ground glass joint and were agitated at 120 rpm for predetermined time intervals at 25°C in a mechanical shaker. At the end of the agitation, the suspensions were filtered through medium paper filters. Langmuir and Freundlich isotherms studies were carried out with different initial concentrations of Hg(II) from 2 to 200 mg Hg/l while maintaining the adsorbent dose at 20 mg/50 ml for 2 h. The effect of agitation time and pH on Hg(II) removal was studied, using 20 mg of resin dose and Hg(II) concentrations of 6 mg/l. All experiments were made 3 times.

Column adsorption was carried out in an 8 mm i.d. columns filled with the resin up to 160 mm. The electrolytic brine taken from the chlor-alkali industry (mercury-cathode method), whose concentration of mercury and pH were 6 mg Hg/l and 4–9 respectively, was passed continuously from top to bottom at a flow rate of 2, 5, 10, 20, or 40 BV/h (bed volume per hour), and 25-ml eluates were collected. Next, the brine saturated with 1000 mg Hg/l, pH of 4–9 and temperature of 22–25°C or 50°C was continuously passed downwards with a flow velocity of 10 BV/h. Each test was repeated twice. Since the brine contained available chlorine, it was treated with $NaHSO_3$ prior to being introduced on the bed in order to reduce the chlorine amount. Desorption studies were carried out as follows: the mercury loaded resin was washed with distilled water. Next, the regenerating medium: 36% HCl or 12% HNO_3 (for cation exchangers) or 5 and 20% NaOH (for anion exchangers) was passed continuously from top to bottom at a flow rate of 1 and 2 BV/h. Resins: Lewatit Mono Plus TP 214 and Purolite S920 are not regenerable and were submitted for Toxicity Characteristic Leach Procedure (TCLP).

Mercury concentration was determined by cold vapor atomic absorption spectrometry.

RESULTS

Adsorption Isotherms

The study of adsorption isotherm is helpful in determining the maximum adsorption capacity of adsorbate for a given adsorbent. The correlations between the equilibrium adsorption of a given ion exchanger – q_e[mg/g] and mercury concentration in the solution – c_e[mg/l] are graphically depicted in Fig. 1. Adsorption was calculated using the formula:

$$q_e = \frac{c_0 - c_e}{m_s} V_0$$

where: c_0 initial concentration of mercury in the solution [mg/l], V_0 volume of the solution [l], m_s mass of ion exchanger [g].

Adsorption isotherms were regular, positive, and concave to the concentration axis for all ion exchange resins (Fig. 1). For resins: Purolite A 500 and Lewatit Mono Plus TP 214, initially the adsorption was rapid but then slowly reached equilibrium at high concentrations. As can be seen in Fig. 1 and according to the slope of the initial portion of the curve, those isotherms were classified as L type of Giles et al.'s classification (31). This indicated that Hg(II) was strongly bound on the resin samples, and that there was no competition from the solvent for ion exchange sites. The isotherms obtained for residual resins may be classified as type S according to Giles classification (31).

It has been found that the experimental data satisfy the equation of Freundlich adsorption isotherms:

$$q_e = k c_e^{1/n}$$

This may be expressed linearly as:

$$\log q_e = \log k + 1/n \log c_e$$

where: k and 1/n – empirical constants (Freundlich parameters): constant k serves as an indicator of the adsorption capacity, and constant 1/n shows the intensity of adsorption in a given system (32).

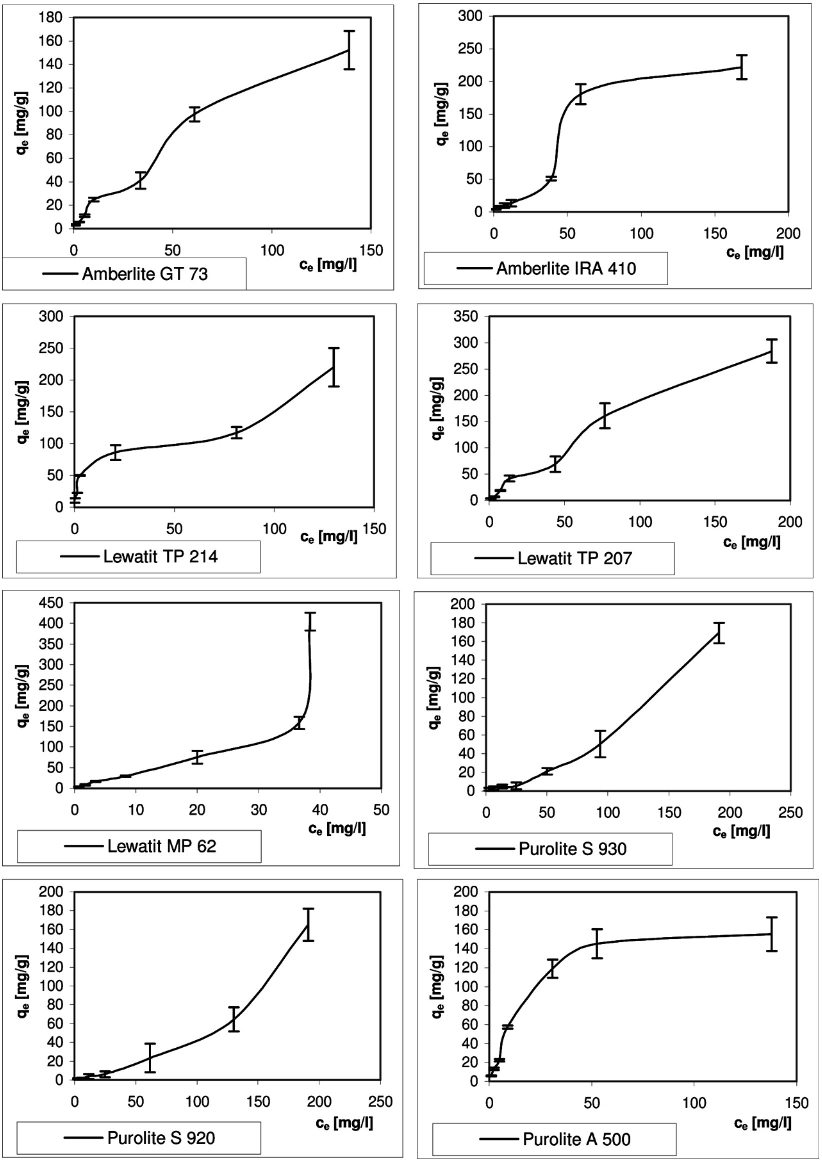


Figure 1. Adsorption isotherms of mercury on ion exchange resins at temperature of 25°C.

The parameters of the Freundlich isotherm equation are equal to the intersection point and the coefficient of the slope of the straight line for the dependence of $\log q_e$ on $\log c_e$. Table 2 shows the constants of the

Table 2. Parameters of the Freundlich and Langmuir equations

Resin name	Freundlich k [mg/g]	n	R^2	Langmuir A	B	R^2	R_L $c_0 =$ 10 mg/l
Amberlite GT 73	3.4498	1.3084	0.9769	31.84713	0.1538	0.8959	0.3939
Amberlite IRA 410	2.4183	1.1203	0.9349	42.01681	0.0788	0.9321	0.5593
Lewatit MonoPlus TP 214	26.7980	2.6199	0.9659	40.81633	11.1364	0.8117	0.0089
Lewatit TP 207	3.488	0.9672	0.9798	55.5556	0.0728	0.9146	0.5787
Lewatit MP 62	4.3393	0.9427	0.9578	142.8571	0.0329	0.9983	0.7523
Purolite S 930	0.8135	1.1792	0.9935	16.0000	0.0549	0.8646	0.6456
Purolite S 920	0.2350	0.8618	0.9694	29.1545	0.0136	0.9609	0.8801
Purolite A 500	8.2732	1.4489	0.9420	151.5152	0.0471	0.9927	0.6799

equation for each ion exchange resin. Correlation coefficients R^2, which were all over 0.9, show that the Freundlich equation describes the adsorption systems well. The approximate capacities of the monolayer (k) determined in the tests indicate that the Hg specific chelating resin with thiourea functional groups—Lewatit Mono Plus TP-214—is the most promising in removing mercury(II) from the 25% solution of sodium chloride. Ion exchange adsorption capacity equals 26.8 mg/g. The k values for the adsorption of Hg(II) on Hg selective cation exchanger with thiol groups, Amberlite GT 73, and on anion exchangers—Purolite A 500, Lewatit MP 62, Amberlite IRA 410 with ammonium active centers and weakly acidic cation exchanger, Lewatit TP 207, were found to be in the range of 2–9 mg/g (Table 2). According to Treybal (33) it has been shown, using mathematical calculations, that *n* values between 1 and 10 represent beneficial adsorption for all the resins tested except for Lewatit MP 62, Lewatit TP-207, and Purolite S 920.

The adsorption data exhibit a Langmuir type isotherm which can be described by the following equation:

$$q_e = A\frac{Bc_e}{1 + Bc_e}$$

where A and B are the Langmuir constants related to the adsorptive capacity and energy of adsorption. The equilibrium adsorption data was fitted to the linear form of the Langmuir equation and the adsorption parameters of the adsorbents were determined as shown in Table 2. In all cases, the correlation coefficients (R^2) for the linear regression fits were found to be>0.8. The adsorption capacities of anion exchangers Purolite A 500 and Lewatit MP 62 (151.5 mg/g and 142.9 mg/g respectively) were greater than that of the others (below 56 mg/g). The equation constants calculated for each adsorption system are given in Table 2.

The essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R_L which is defined by:

$$R_L = \frac{1}{1 + Bc_0}$$

According to Hall et al. (34), the R_L values between 0 and 1 at different concentrations indicate favorable adsorption of Hg(II) on the resins tested (Table 2).

Effect of pH

The effect of pH on Hg(II) removal was studied, using 20 mg of resin dose and Hg(II) concentrations of 6 mg/l in 25% NaCl solution at pH 3, 7, and 11, temperature of 25°C and agitation time of 2 hours. Figure 2 shows the effect of pH on the Hg(II) amount adsorbed at equilibrium by ion exchange resins. It is clear that Amberlite IRA 410, Lewatit Mono Plus TP 214, Lewatit MP 62, and Purolite S 930 are effective for the quantitative removal of Hg(II) over the entire range of pH tested (3–11). Amberlite GT 73, Lewatit TP 207, and Purolite S 920, however, are effective at high pH, Purolite A 500 at low pH.

Effect of Agitation Time

The effect of agitation time on Hg(II) removal was studied, using 20 mg of resin dose and Hg(II) concentrations of 6 mg/l in 25% NaCl solution

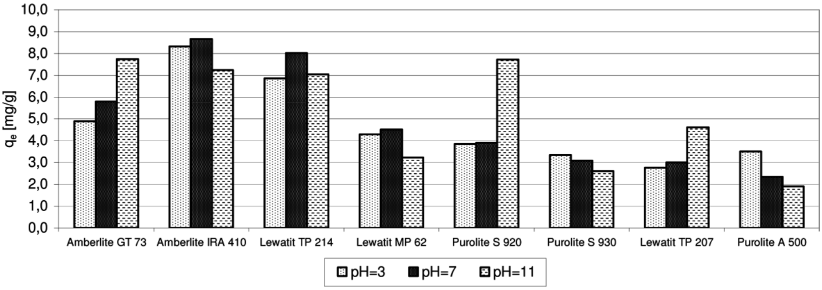


Figure 2. Effect of pH on mercury adsorption on ion exchange resins.

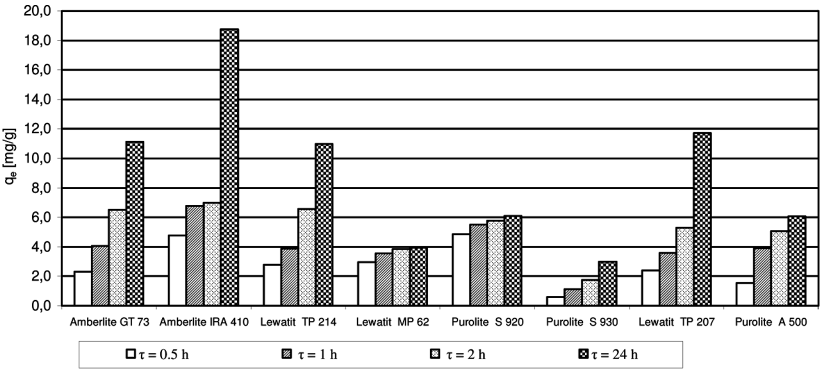


Figure 3. Effect of agitation time on mercury adsorption on ion exchange resins.

at pH 3.7, temperature of 25°C, and agitation time of 0.5, 1, 2, and 24 hours (Fig. 3). The amount of Hg(II) adsorbed increased with the agitation time and attained equilibrium at about 2 hours for Lewatit MP 62 and Purolite S 920 and 24 hours for the others.

Column Mode

Influence of Flow Rate

The electrolytic brine whose concentration of mercury and pH were 6 mg Hg/l and 4–9 respectively was passed continuously from top to bottom at a flow rate of 2, 5, 10, 20, or 40 BV/h (bed volume per hour). The effect of the mercury removal from the electrolytic brine in the column system is presented in Fig. 4 as a dependence of mercury concentration in the effluent from the column–c [μg/l] on the flow rate of solution through the bed – v[BV/h]. It has been found that mercury concentration in the brine decreased from 6 mg/l to 2.6, 8.6, 10.4, 15.9, 17.9, 50.7, 99.0, and 475.3 μg/l, at a flow of 2 BV/h, using resin Purolite S 920, Purolite A 500, Amberlite IRA 410, Amberlite GT 73, Lewatit Mono Plus TP 214, TP 207, Purolite S 930, and Lewatit MP 62 respectively. At a flow rate of 10 BV/h (recommended by the resins manufacturers) mercury concentration in the effluent from the column ranged from 5.6 μg/l to 26 μg/l for all resins tested, except Lewatit MP 62, TP 207 and Purolite S 930. The results yielded indicate the possibility of purifying the brine below the standard of 50 μg/l imposed by regulations, using the simplest system of one ion exchange column.

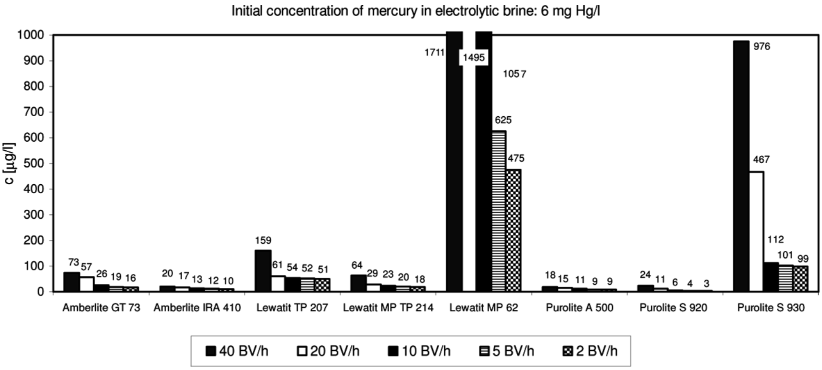


Figure 4. Influence of flow rate on average mercury concentrations achieved by ion exchange resins at temperature of 22–25°C.

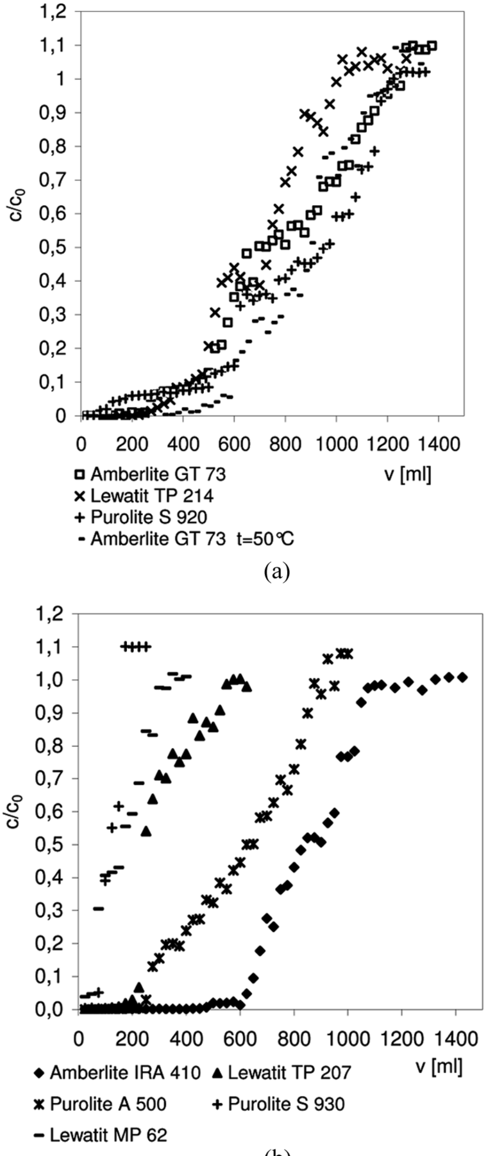
Breakthrough Curves

This part of the study was aimed at finding capacities of the resins tested: effective one (at breakthrough point) and total one (at the point of bed exhaustion). The loading of resins at low concentration of the feed solution prolongs the work cycle and prevents continuous loading. Therefore, the brine was concentrated with mercury(II) solution up to 1 g/l. The loading was carried out in the columns of identical dimensions always filled with the same volume of the bed. The brine adjusted to a specific pH (established in the previous research) was passed at a stable rate of 10 BV/h, at a temperature of 22–25°C. The loading of Amberlite GT 73 was conducted at 50°C as well.

The effectiveness can best be determined by measuring the fraction of mercury that passes through a resin as a function of the feed solution volume. The initial breakthrough fraction (f_s) was equal to:

$$f_s = \frac{c}{c_0}$$

where c – concentration of mercury in the effluent (µg/l). Figure 5 shows the mercury breakthrough for each ion exchange resin. The breakthrough curves assumed a characteristic S shape, except for the breakthrough curves for Lewatit TP 207, MP 62, and Purolite S 930 which indicate a fast breakthrough and saturation of the bed. The ion exchange capacities calculated for all ion exchangers are given in Table 3. They clearly show that the anion exchanger Amberlite IRA 410 at 25°C and Hg selective resin Amberlite GT 73 at 50°C are the



(a)

(b)

Figure 5. Mercury breakthrough curves on different ion exchange resins. a) Results on Amberlite GT 73, Lewatit Mono Plus TP 214 and Purolite S 920; b) Results on Amberlite IRA 410, Lewatit TP 207, Lewatit MP 62, Purolite A 500 and Purolite S 930.

Table 3. Effective and total capacities of ion exchange resins, a_E effective capacity of ion exchanger, v_E volume of effluent collected up to break-through, a_T total capacity of ion exchanger, v_T volume of effluent collected upon exhaustion of bed, BV bed volume, C_0 influent concentration of Hg ion

	Break-through point		Exhaustion point					
Resin name	a_E [g/l]	v_E [ml]	a_T [g/l]	v_T [ml]	BV [ml]	c_0 [mg/l]	pH	Temp. (°C)
Amberlite GT 73	29.3 ± 2.2	275	101.9 ± 7.5	1175	8.0	853 ± 8	8.0	24
Amberlite GT 73	79.5 ± 6.1	550	141.9 ± 10,9	1150	8.0	1156 ± 12	8.0	50
Amberlite IRA 410	101.7 ± 5.2	650	151.5 ± 7.7	1100	6.5	1017 ± 10	4.5	24
Lewatit MonoPlus TP 214	56.8 ± 2.6	375	122.6 ± 5.6	1000	8.0	1211 ± 11	7.1	24
Lewatit TP 207	41.8 ± 2.2	225	75.7 ± 3.9	550	8.0	1485 ± 13	9.0	24
Lewatit MP 62	7.3 ± 0.4	50	30.6 ± 1.5	300	8.0	1161 ± 12	4.5	22
Purolite S 930	10.4 ± 0.6	75	17.7 ± 1.1	175	7.8	1082 ± 10	4.4	25
Purolite S 920	23.7 ± 1.04	175	136.1 ± 6.0	1200	8.0	1082 ± 10	9.4	24
Purolite A 500	43.5 ± 2.1	275	113.7 ± 5.6	875	7.1	1120 ± 9	4.5	24

most capacious for mercury(II) ion. Their total capacities are 152 and 142 g/l respectively. Very good results were also obtained for Hg specific resins Purolite S 920 ($a_T = 136$ g/l) and Lewatit Mono Plus TP 214 ($a_T = 123$ g/l). Calculations were made utilizing the method described by Michaels (35).

Desorption and Regeneration

The desorption of adsorbed Hg(II) from the spent ion exchange resins was also studied. Resin loaded with the maximum amount of Hg(II) was washed, using 36% HCl or 12% HNO_3 (for cation exchangers) or 5 and 20% NaOH (for anion exchangers) (36–39). The regenerating medium was passed continuously from top to bottom at a flow rate of 1 and 2 BV/h. It can be seen that bound Hg(II) is quantitatively desorbed from the Amberlite GT 73 to the suspending medium and less than 30% of sorbed Hg on the other resins (Fig. 6). Resins: Lewatit Mono Plus TP 214 and Purolite S 920 are not regenerable and were submitted for Toxicity Characteristic Leach Procedure (TCLP). Both resins leached less than regulatory levels of mercury (0.2 mg/l) in the TCLP test.

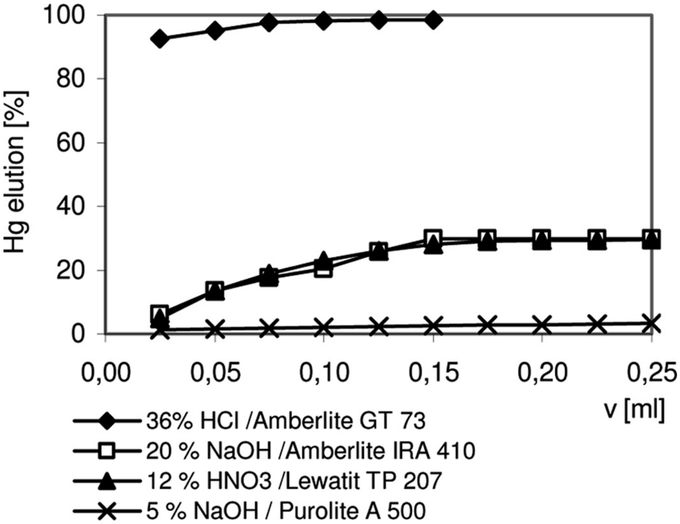
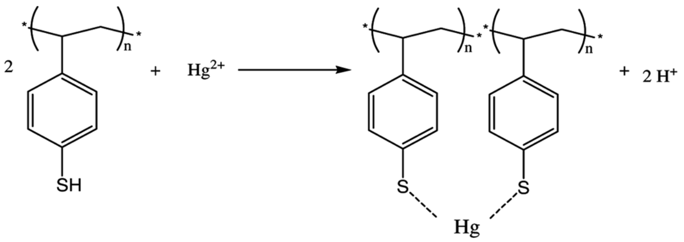


Figure 6. Elution of mercury from some ion exchange resins.

DISCUSSION

The objective of the research (i.e., comparative studies into the removal of mercury ions present in the waste brine produced by mercury electrolysis, using reactive polymers) has been accomplished. Effectiveness of eight ion exchange resins (Table 1) in removing mercury as well as their regeneration and metal recovery were tested. The literature studied revealed that ion exchange resins, notably those showing specific characteristics with respect to Hg(II) ions, are commonly used (27–29). Generally, those resins bind mercury so strongly that the regeneration of resins to be reused is regarded as uneconomical; the cycle time reaches thousands of hours. Such is the case with two macroporous polystyrene chelating resins tested in this study: Purolite S 920 which can be loaded with mercury up to 200 g/l of resin (36) and Lewatit Mono Plus TP 214 containing thiourea groups displaying a strong affinity towards mercury (37). After they are saturated with mercury, the resins must be stored observing local legal regulations. The other resins tested herein i.e., Amberlite GT 73 – weakly acidic cation exchange macroporous polystyrene resin with functional thiol groups (38) can be regenerated according to the manufacturers. Out of the selective resins, Amberlite GT 73 revealed the highest effectiveness, reaching a total capacity of 142 g Hg/l; however, at an elevated temperature of 50°C (at 24°C

$a_T = 102\,g/l$). At room temperature, Purolite S 920 and Lewatit Plus TP 214 are the most effective, capable of being loaded with 136 g and 123 g of mercury per 1 liter of resin. Amberlite GT 73 has a large advantage since it can be regenerated (100% mercury desorption was obtained) and used repeatedly after its reactivation. In this study, almost the same capacity of the resin that it had in the first cycle was confirmed in the second one. It should also be mentioned that thiol groups present in the resin display strong affinity towards mercury following the schematic below (38):

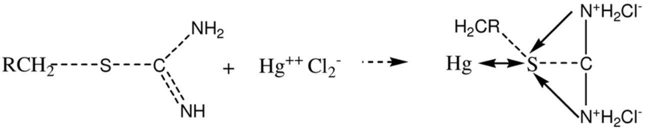


Moreover, mercury occupies the first position in the order of selectivity followed by ions of other metals that might compete with mercury in the loading of resin (38):

$$Hg > Ag > Cu > Pb > Cd > Ni > Co > Fe > Ca > Na.$$

Hg specific resins: Purolite S 920 and Lewatit Mono Plus TP 214 are not regenerable, however, they pass the TCLP test.

As for Purolite S 920, mercury is strongly complexed by sulphonic and nitric groups following the schematic (36):



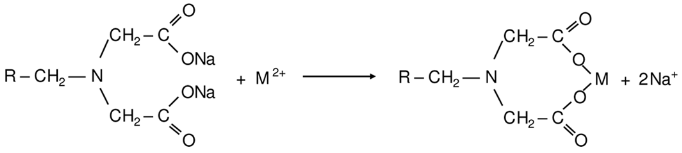
The reaction of mercury(II) ions with Lewatit Mono Plus TP 214 is similar. However, other precious metals present in the form of free cations can also be simultaneously complexed which might decrease the adsorption capacity of mercury.

This study, apart from the resins that selectively interact with mercury, also focused on available cation and anion exchangers. This was caused by the fact that the brine contained various forms of

Hg(II), both anions and cations, which were at thermodynamic equilibrium (27):

$$
\begin{aligned}
&Hg^{2+} + Cl^- \rightleftharpoons HgCl^+\\
&HgCl^+ + Cl^- \rightleftharpoons HgCl_2\\
&HgCl_2 + Cl^- \rightleftharpoons HgCl_3^-\\
&HgCl_3^- + Cl^- \rightleftharpoons HgCl_4^{2-}
\end{aligned}
$$

and this offers the possibility for mercury separation both on cation and anion exchangers. Very good and good results were obtained for strongly basic polystyrenedivinylbenzene matrixes with quaternary functional ammonium groups: Amberlite IRA 410 (152 g/l) and Purolite A 500 (114 g/l). However, it was impossible to regenerate both resins, even by use of 20% NaOH solution. The high effectiveness of anion exchangers and lower or even low effectiveness of cation exchangers in mercury removal from electrolytic brine can be explained by the change in the equilibrium mentioned above that favored chloride complexes as their amount started decreasing in the solution. As for cation exchangers, the ions of the metals present in the brine not forming stable complexes with chloride e.g. Ca^{2+} do not compete with mercury. Such competition probably takes place in the cation exchanger/brine system. A good example here is the macroporous polysteyrene chelating resin containing iminodiacetate groups, Purolite S 930, used to remove the cations of heavy metals from industrial wastewater and which had the smallest total capacity of all the resins tested in the study, 18 g/l. The negative result was probably produced by the fact that there were other ions in the brine which were higher in the order of selectivity than mercury e.g. Ca^{2+} and Fe^{2+} whose concentration was frequently higher than that of mercury and those ions bind first with the functional dicarboxyl group (39):



Experiments showed that, the cation exchange resins were able to extract Ca^{2+}, Fe^{3+} and Al^{3+} ions in low quantity (0.1–10 mg/g). The Hg(II) adsorption on Amberlite GT 73 and strongly basic anion exchangers was selective and no interferences have been observed in the presence of Ca^{2+}, Fe^{3+}, Al^{3+}, SO_4^{2-} ions in small concentrations.

The differences in exchange capacitites obtained for the resins tested, using the static (batch) and dynamic (column) techniques arise from the fact that the batch technique used analytical grade brine while the column tests used electrolytic brine.

CONCLUSIONS

The present study clearly establishes that strongly basic anion exchange resins and some selective exchangers are very effective adsorbents for Hg(II) removal from NaCl concentrated solutions and chlor-alkali industry wastewaters. Removal of Hg(II) from electrolytic brines could be achieved below the concentration of 0.05 mg/l. Amberlite GT 73 loaded with Hg can be regenerated and reused by acid treatment. Spent resins Purolite S 920 and Lewatit Mono Plus TP 214 were classified as non-hazardous waste (EPA TCLP test). The regeneration of Amberlite IRA 410 requires, however, further investigation.

The novelty of the presented paper lies in the reports of efficient mercury removal from concentrated NaCl solution and electrolytic brine, two very specific and unpredictable media due to their high salinity and its resulting high ionic strength. To date the above have not been reported in the literature, despite the strong demand from the chlor-alkali industry.

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