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ION EXCHANGE RESINS OF INCREASED SELECTIVITY TOWARDS ARSENIC

Model solutions the composition of which (ionic form and concentration of arsenic and total salinity) corresponds to that of wastewater from a copper production plant were used in this study. The behaviour of strong base microporous anion exchangers Amberlite IRA-938, Varion ATM and Wofatit SZ-30 treated with a Na_2S solution was investigated. The data obtained show that the sulfide-regenerated resins are characterized by a higher selectivity towards arsenic.

On the basis of 2^{6-2} statistical design, it has been proved that ion exchange capacity depends on the pH of treated water and the specific loading at exhaustion period. The optimum levels of the significant variables were determined by means of experiments on 3^n factorial design.

1. INTRODUCTION

So far, ion exchange method for arsenic removal from aqueous solutions has been successfully applied only to wastewaters with low concentration of background electrolyte (low total salinity) [1], [6].

This fact can be explained by the extremely low selectivity of both strong and weak base anion exchangers towards the ionic forms of arsenic in water (pH > 4).

Preliminary experiments showed that at pH = 3 the specific thio-resin IMAC TMR could sorb selectively 7.0 to 7.5 g of arsenic per 1 dm^3 of the resin.

These results have inclined us to investigate the possibility of a selective arsenic removal from wastewaters by strong base anion exchange resins treated with a Na_2S solution. This approach is similat to that for selective removal of mercury from wastewaters by conventional anion exchangers treated with Na_2S as previously described [4].

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2. EXPERIMENTAL

In the present study we have used a model composition of water solution (i.e., ion form and concentration of arsenic and total salinity) which corresponds to that of wastewaters from a copper production plant (tab. 1).

Table 1

Model water solution composition

Reagent	Concentration
Na_2AsO_3	50 mg As/dm^3
NaCl	1400 mg Cl^-/dm^3
Na_2SO_4	50 mg SO_4^{2-}/dm^3

The behaviour of strong base macroporous anion exchangers Amberlite IRA-938, Varion ATM and Wofatit SZ-30 was studied under dynamic conditions. The water solution was filtered down-flow in a glass column (diameter 20 mm) through a 50 cm^3 layer of the suitable resin. Influent and effluent concentrations of arsenic were determined photometrically making use of the specific reaction of arsenic with AgDDK (Ag-diethyldithiocarbamate).

The conditioning of the resin comprised several operations:

1. Treatment with a 5% aqueous solution of Na_2S (at the corresponding specific consumption of reagent) with and without the addition of alkalizing agent (NaOH).
2. Washing the layer with two bed volumes of distilled water.
3. Treatment with a sodium chloride solution at the corresponding specific consumption and concentration (in some cases only).

The effects of feed water pH (z_1), specific consumption of alkali sulfide reagent (z_2)*, amount of alkalizing reagent (z_3), specific consumption (z_4) and concentration (z_5) of sodium chloride used as a reagent controlling the sulfur content in the ion exchange phase, and that of the specific loading in the exhaustion period (z_6) on the resin capacity (Y) were studied.

The performed experiments were based on 2^{6-2} factorial design with z_1, z_2, z_3, z_4, z_5, and z_6, each at two levels. The values of these factors and the response obtained in various experimental runs (for Amberlite IRA-938) are presented in tab. 2.

These data were fitted to the response function:

$$\hat{Y} = f(x_1, x_2, x_3, x_4, x_5, x_6) = b_0 + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_4 x_4 + b_5 x_5 + b_6 x_6 \quad (1)$$

* Preliminary experiments showed that at relative consumption lower than 50 g of Na_2S/dm^3 (5% solution) the resin capacity regarding arsenic decreases progressively.

Table 2

Levels of factors and the responce of statistical design experiments (for Amberlite IRA-938)

Exp. runs	Factors						Y
	z_1 pH units	z_2 g/dm^3 resin	z_3 g/dm^3	z_4 g/dm^3 resin	z_5 g/dm^3	z_6 dm^3/dm^3·h	g As/dm^3 resin
1	7	200	10	200	50	30	0.00
2	2	200	10	0	10	30	3.04
3	7	50	10	200	50	30	0.00
4	2	50	10	0	10	30	1.99
5	7	200	0	200	10	30	0.00
6	2	200	0	0	50	30	2.86
7	7	50	0	200	10	30	0.00
8	2	50	0	0	50	30	2.66
9	7	200	10	0	10	10	0.92
10	2	200	10	200	50	10	0.50
11	7	50	10	0	10	10	1.24
12	2	50	10	200	50	10	0.28
13	7	200	0	0	50	10	0.83
14	2	200	0	200	10	10	0.55
15	7	50	0	0	50	10	1.05
16	2	50	0	200	10	10	0.76

when variables stand for the following ratios:

$$x_1 = \frac{z_1 - 4.5}{2.5}, \quad x_2 = \frac{z_2 - 125}{75}, \quad x_3 = \frac{z_3 - 5}{5},$$
$$x_4 = \frac{z_4 - 100}{100}, \quad x_5 = \frac{z_5 - 30}{20}, \quad x_6 = \frac{z_6 - 20}{10}. \tag{2}$$

The constants $b_0, b_1, \ldots, b_6$ were evaluated by the least squares method. The values of the coefficients and the t-criterion are given in tab. 3. The variance of the experiment $S_e^2 = 0.0319$. This value was obtained from five replications carried out in the center of the design ($x_i = 0$).

The test of the statistical significance of the coefficients at a critical value of t ($t_{tabl(0.05,3)} = 3.18$) shows that b_0, b_1, b_4 and b_6 are significant coefficients. Hence, it may be concluded that the capacity of Amberlite IRA-938 is strongly influenced by the factors z_1, z_4 and z_6.

It has been assumed that the data, on the basis of which the significant factors were determined, are also valid for Wofatit SZ-30 and Varion ATM.

The application of this approach is fully justified, as these resins are of the same dissociation and structural type (strong base and macroporous).

The optimum levels of the significant variables, i.e., feed water pH (z_1) and specific loading in exhaustion period (z_6), each at 3 levels, were determined from experiments based on 3^n statistical design. Since at zero concentration of NaCl, capacity (z_4) reaches its maximum, it was excluded from further experiments.

The insignificance of the z_2 and z_3 factors makes it possible to conduct our subsequent experiments at lower levels of these factors (i.e., at 50 g of 100% Na_2S/dm^3 resin and without NaOH, respectively).

The 3^n factorial design was chosen because information obtained from it concerns both linear and quadratic components of the effects of the factors. The quadratic component may imply the maximum or minimum response at the same intermediate factor combination or at a point outside the range examined for some or all the factors, indicating a need for further work at a different set of levels [3]. Moreover, this design is quasi *D*-optimum and it allows us to obtain more precise estimations of the regression coefficients.

The actual values of the variables corresponding to the coded values are shown in tab. 4. Table 5 shows the resin capacities (Y_i).

The results for the resin capacity at different values of z_1 and z_6 were fitted to the response function:

$$\hat{Y}_i = f(x_1, x_2) = A_0 + A_1 x_1 + A_2 x_2 + A_{12} x_1 x_2 + A_{11} x_1^2 + A_{22} x_2^2, \quad i = 1, 2, 3 \quad (3)$$

Table 3

Variables	x_0	x_1	x_2	x_3	x_4	x_5	x_6
b_i	1.04	3.12×10^{-1}	4.36×10^{-2}	-4.38×10^{-2}	-7.81×10^{-1}	-2.12×10^{-2}	-2.78×10^{-1}
t_i	23.31	6.98	0.97	0.98	17.48	0.47	6.21

Table 4

Levels of feed water pH and specific loading in exhaustion period

Factors	Upper level +1	Base level 0	Lower level −1	Unit
Feed water pH, z_1 (x_1 in coded form), pH units	4	3	2	1
Specific loading in exhaustion period, z_6 (x_2 in coded form), $dm^3/dm^3 \cdot h$	30	20	10	10

where x_1 and x_2 are the coded forms for

$$x_1 = \frac{z_1 - 3}{1}, \quad x_2 = \frac{z_6 - 20}{10}. \tag{4}$$

The constants A_0, A_1, A_2, etc, were evaluated using the least squares method. By substituting them in eq. (3) we get regression models presented in tab. 6. The standard deviations as well as the calculated and critical values of the F-criterion are also shown.

Table 5

The response of statistical design experiments

Exp. runs	z_1 pH units	z_2 $dm^3/dm^3 \cdot h$	Resin capacity (g As/dm^3 resin)		
			Amberlite IRA-938 Y_1	Varion ATM Y_2	Wofatit SZ-30 Y_3
1	2	10	0.47	4.37	0.97
2	2	20	0.89	4.56	2.10
3	2	30	0.76	4.94	1.15
4	3	10	3.30	5.32	5.91
5	3	20	4.90	5.64	6.50
6	3	30	1.63	4.86	5.67
7	4	10	1.52	5.20	5.08
8	4	20	1.52	4.40	5.18
9	4	30	1.84	4.50	5.41

Table 6

Regression models, standard deviations and F-criterion

Resin	Mathematical models	Standard deviation	$F_{calc.}$	$F_{crit.}$ $\nu_1 = 3$, $\nu_2 = 3$, $\alpha = 0.05$
Amberlite IRA-938	$\hat{Y}_1 = 3.843 + 0.457x_1 - 0.178x_2 - 2.109x_1^2 + 8.999 \times 10^{-3} x_1 x_2 - 0.850x_2^2$	0.4917	7.58	9.28
Varion ATM	$\hat{Y}_2 = 5.274 + 3.830 \times 10^{-2} x_1 - 9.833 \times 10^{-2} x_2 - 0.612x_1^2 - 0.317x_1 x_2 - 1.666 \times 10^{-3} x_2^2$	0.1811	1.03	9.28
Wofatit SZ-30	$\hat{Y}_3 = 6.401 + 1.908x_1 + 4.499 \times 10^{-2} x_2 - 2.712x_1^2 + 3.750x_1 x_2 - 0.562x_2^2$	0.4126	5.33	9.28

In all the cases., $F_{calc.}$ is lower than $F_{crit.}$ and it can be concluded that the mathematical models adequately describe the process under study.

Calculations for the different resin capacity can be performed by assigning arbitrary values for x_2 in the equations given in tab. 6 and then by solving the resulting quadratic equations for x_1. This is shown in figs. 1–3 corresponding to Amberlite IRA-938, Varion ATM and Wofatit SZ-30, respectively.

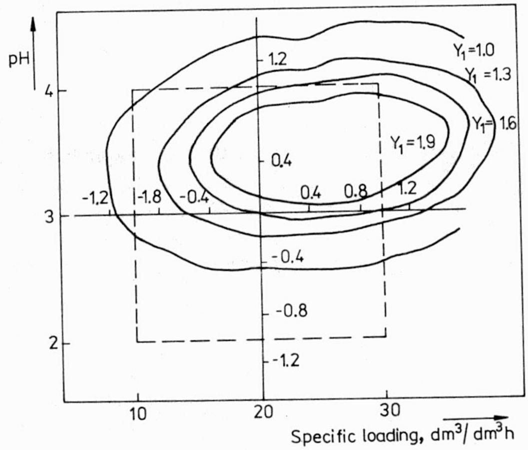

Fig. 1. Constant level capacity curve for Amberlite IRA-938 (the interrupted line denotes the experimental range)

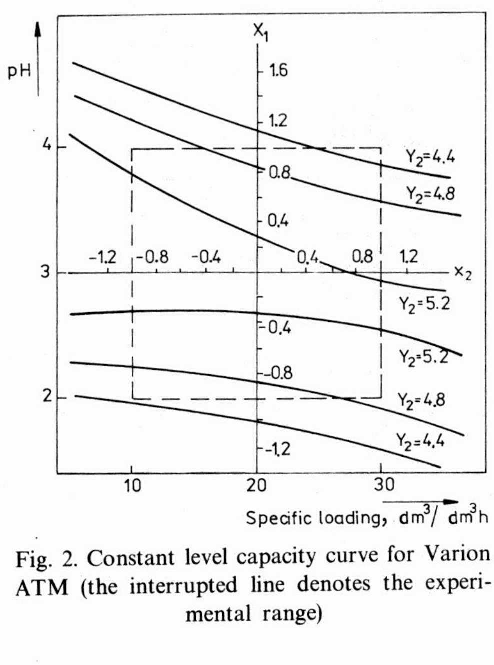

Fig. 2. Constant level capacity curve for Varion ATM (the interrupted line denotes the experimental range)

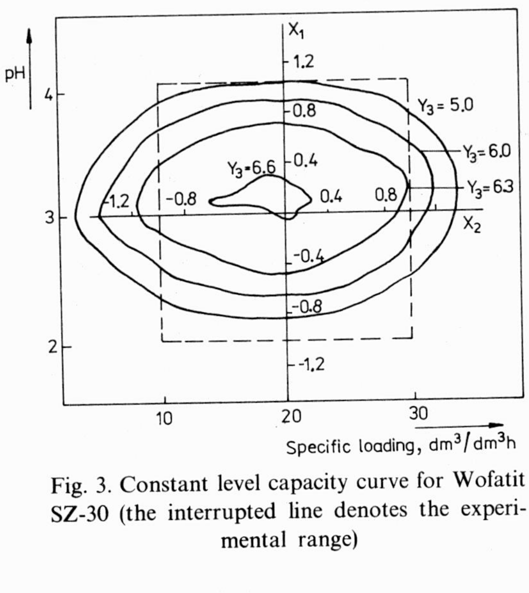

Fig. 3. Constant level capacity curve for Wofatit SZ-30 (the interrupted line denotes the experimental range)

Figures 4–6 depict the variation of resin capacity at various values of feed water pH. They show that the capacity of every resin reaches a maximum. The conditions for the optimum capacity were obtained according to the method by Box (complex algorithm) [2].

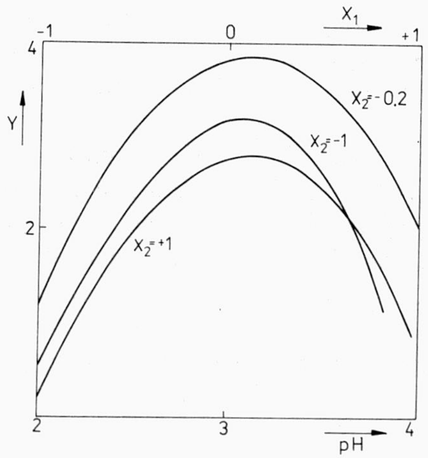

Fig. 4. pH-capacity relation at fixed value of specific loading at exhaustion (for Amberlite IRA-938)

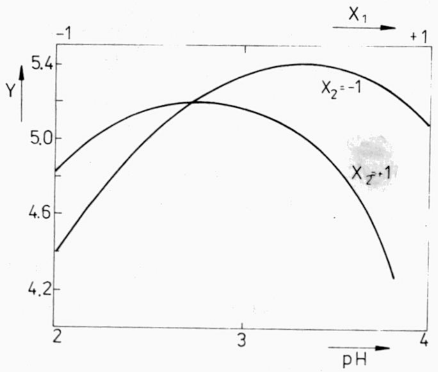

Fig. 5. pH-capacity relation at fixed value of specific loading at exhaustion (for Varion ATM)

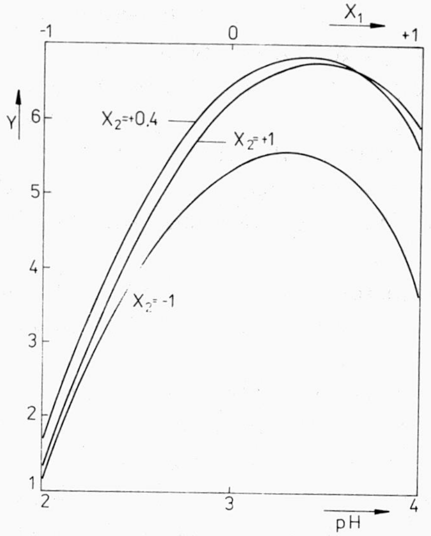

Fig. 6. pH-capacity relation at fixed value of specific loading at exhaustion (for Wofatit SZ-30)

3. DISCUSSION

As these experiments have shown, the resin capacity was not considerably affected by increase in the specific consumption above 50 g of Na_2S (100%)/dm^3 resin. It has been found that the ability of modified resin (converted sufficiently into a sulfide ion form) to sorb arsenic ions depends on pH of the treated water and on the specific loading at exaustion period.

The analysis of the model equations for the corresponding resins (given in tab. 6) shows that the pH of the influent can be the more significant factor. In view of that fact, the relation between pH and the capacity was studied at fixed values for the specific loading at exhaustion (figs. 4–6). The obtained optimum values of the process parameters show that the optimum pH for the three resins is within a relatively narrow range (3.2–3.5).

The demand regarding pH influent is obviously associated with the necessity of converting arsenic into its cationic form (As^{3+}) suitable for the arsenic–sulfur interaction.

The optimum values for the exhaustion and specific loading differ more considerably being 18 and 24 $dm^3 \cdot (dm^3)^{-1} \cdot h^{-1}$ for Amberlite IRA-938 and Wofatit SZ-30, respectively. The data obtained for Varion ATM are of some interest. In the examined pH interval two extrema for Y are obtained (at pH = 2.0–2.6 and specific loading = 30 $dm^3 \cdot (dm^3)^{-1} \cdot h^{-1}$; and at pH = 2.7–4 and specific loading = 10 $dm^3 \cdot (dm^3)^{-1} \cdot h^{-1}$). These results confirm the logically inferred demand for a lower volume rate of exhaustion at higher pH of the influent.

The differences between the sulfide-treated strong base anion exchangers having the same dissociation characteristics are probably due to structural differences (predominant pore size, pore volume and specific area).

That supposition is based on the data concerning the strong influence of the structure of microporous anion exchange resins on the sortpion and sulfide desorption of mercury [5]. That problem will be the subject of subsequent investigations.

The data for the tested resins (evaluation was done on the capacity basis only) show that the most suitable resin is Wofatit SZ-30 (maximum capacity = 6.6–6.9 g As/dm^3 resin).

The "constant level capacity curves" (figs. 1–3) are of particular importance. They may be used to obtain two different pairs of parameters (pH influent and specific loading at exhaustion) at which the capacity is the same. This relationship may be quite useful in treating wastewaters with different pH since, in order to reach a desired capacity value, a suitable value for the specific loading can be found without pH adjustment.

4. CONCLUSIONS

The principle possibility of selective sorption of arsenic by strong base microporous anion exchangers treated with an aqueous solution of alkali sulfide was studied.

Based on the experiments and the modelling of the sorption processes, the significant factors and their optimum values for reaching the maximum sorption capacity were evaluated.

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ŻYWICE JONOWYMIENNE O PODWYŻSZONEJ W STOSUNKU DO ARSENU SELEKTYWNOŚCI

Zastosowano roztwory modelowe, których skład (formy jonowe, stężenie arsenu i ogólne zasolenie) odpowiada ściekom z huty miedzi. Badano zachowanie się silnie zasadowych wymieniaczy anionowych: Amberlitu IRA-938, Varionu ATM i Wofatitu SZ-30 zadanych roztworem siarczku sodowego.

Z otrzymanych danych wynika, że żywice regenerowane siarczkiem odznaczają się większą selektywnością wobec arsenu. Na podstawie doświadczenia czynnikowego 2^{6-2} stwierdzono, że pojemność jonowymieniacza żywicowego zależy od pH oczyszczanej wody i od właściwości ładunku w okresie wyczerpania. Optymalne poziomy istotnych zmiennych wyznaczono na podstawie doświadczeń czynnikowych 3^n.

ИОНООБМЕННЫЕ СМОЛЫ С ПОВЫШЕННОЙ ПО ОТНОШЕНИЮ К МЫШЬЯКУ СЕЛЕКТИВНОСТИ

Применены модельные растворы, состав которых (ионные формы, концентрация мышьяка и общая засоленность) соответствует сточным водам от медеплавильного завода. Исследовалось поведение сильнощёлочных анионитов: амберлита IRA-938, вариона АТМ и вофатита SZ-30 заданных раствором сульфида натрия.

Из полученных данных следует, что смолы, регенерированные сульфидом, отличаются большей селективностью по отношению к мышьяку. На основе реактивного опыта 2^{6-2} было отмечено, что ёмкость смоляного ионообменника зависит от pH очищенной воды и от соответствующего количества в период исчерпания. Оптимальные уровни свободных переменных были определены на основе реактивных опытов 3^n.