Application of Chitosan to Cobalt Recovery: Evaluation by Factorial Design of Experiments

I. BLAZQUEZ, F. VICENTE, and B. GALLO, *Departamento de Química Analítica,* and I. ORTIZ and A. IRABIEN,* *Departamento de Química Técnica, Facultad de Ciencias, Universidad Pais Vasco, Apdo. 644, Bilbao, Spain*

Synopsis

A natural polymer in a commercially available form (chitosan) has been tested using a factorial design of experiments for its application to cobalt recovery either in hydrometallurgy and in analytical separations. A simple mechanically stirred system has been used, evaluating the influence of the contact time, iron (II), cobalt (II), chitosan concentration, salinity, and pH in the separation. The pH value has a dramatic influence on the metal recovery from a negligible amount of metals at pH = 1.0 to a quantitative sorption at pH = 3.0. Linear relationships between sorbed metal and the variables have been determined at constant pH value and a quantitative evaluation of the metal recovery at different pH values can be performed using the maximum sorption capacity of the chitosan (a_0) and the selectivity for both metals. The obtained results allow the evaluation of the recovery of metals using chitosan as solid phase.

INTRODUCTION

The rising world prices for metals coupled with the introduction of strict regulations against the pollution of the environment have focused attention on the recovery of metals from lean ores and wastes. Two main types of processes play a leading role in this separation: (i) metal extraction based on liquid–liquid contact processes[1] and (ii) liquid–solid contact processes[2] in which the metal is precipitated from a solution or adsorbed on a solid matrix.

In the second type of processes, i.e., solid–liquid contact systems, complex phenomena take place due to the physicochemical interactions between the phases present in the contact medium, making difficult the analysis and modelling of the process. Some typical cases, such as adsorption by active carbon or by alumina,[3] ion exchange by synthetic polymers,[4-6] etc., have been successfully described in the literature; however, very little is known on the complex phenomena occurring between solid membranes formed by natural polymers, e.g., chitin membranes or its deacetylated derivative, chitosan membranes, and the liquid phase containing metal ions.[7-12]

The special characteristics of chitosan membranes[9,13-16] have led to their application to chromatographic separations,[17-21] showing considerable advantages on comparison with results obtained with chitin membranes, substituted cellulose, and/or some polyaminic polymers.[17,22]

---

*Author to whom correspondence should be addressed.

For this reason some of the phenomena taking place in the interaction polymer-metal ion, such as adsorption, ion exchange, complexation, precipitation, coprecipitation, entrapment, etc. have been widely studied,[17,18,20,23,24] pointing out the considerable difficulty of the analysis and modelling of systems where chitosan membranes are considered for chromatographic separations or in hydrometallurgy. A considerable number of variables must be analyzed: (i) variables related to the physicochemical composition of the solid, i.e., physical shape, grain size, specific surface; (ii) variables related to the liquid phase, i.e., pH, concentration of cations and anions, and oxidation state of the metals; (iii) variables related to the contact, i.e., stirred system, system with dispersion, temperature evolution, etc.[15,17,18,20,25]

For this reason in order to establish the viability of the application of chitosan membranes to metal recovery from lean ores and wastes, it should be advisable to study the behavior of the system from a design of experiments established in advance, determining the range of suitable variables for the industrial operation.

In the present work the behavior of the system chitosan–Fe(II)–Co(II) working in a stirred system has been studied. The influence of the variables: contact time, pH, salinity (sodium sulfate), initial concentrations of the commercial chitosan, iron, and cobalt on the process have been studied by means of a factorial design of experiments.

Separation processes of metals have great interest in analytical and applied chemistry because of the frequent appearance of similar systems in hydrometallurgy. A statistical design of experiments is a useful tool for the study of such a system where a considerable number of complex phenomena and variables have to be considered simultaneously.

EXPERIMENTAL

Commercially available chitosan from Bioshell, Inc. was used in the present work. Specifications were: flat-shaped angular particles; particle size distribution 8 mesh 0.5%, 8–12 mesh 24.5%, 12–16 mesh 31%, 16–20 mesh 15.5%, 20–30 mesh 10%, 30–50 mesh 7.5%, 50 mesh 11%; moisture, 6–10%; ash 0.5%; maximum protein 0.5%, maximum N 8%; NH_2 7.5–8.2%; % deacety lation 77–83%; bulk density 0.288 cc; chloride 0.54%; sodium 0.24%; Pb (< 10 ppb), Ag (< 10 ppb), total of As, Ag, Bi, Cd, Cu, Hg, Pb, Sb, and Sn less than 5 ppm.

All the reagents used in the preparation of solutions were Analar grade. The concentration of iron and cobalt were measured by atomic absorption spectrometry.

The experimental procedure was as follows: Synthetic solutions with fixed values of the initial pH and initial concentrations of Co(II) and Fe(II) were prepared. Known amounts of the solution and chitosan were put together into the experimental flask, and the stirring was started. At the end of each experiment the solid and liquid phases were separated by vacuum filtration and the amount of Fe(II) and Co(II) in the solution was determined. Combustion of the organic matrix was carried out at 700°C for 2 h; after this time the residual solid was solved with hydrochloric acid in order to analyze the metals in the membrane.

TABLE I
Factorial Design

Expt no.	x_1	x_2	x_3	x_4	x_5	x_6
1	−	−	+	+	+	+
2	+	−	−	+	+	+
3	+	−	+	−	+	+
4	+	−	+	+	−	+
5	+	−	+	+	+	−
6	−	−	−	−	+	+
7	−	−	−	+	−	+
8	−	−	−	+	+	−
9	−	−	+	−	−	+
10	−	−	+	−	+	−
11	−	−	+	+	−	−
12	+	−	+	−	−	−
13	+	−	−	+	−	−
14	+	−	−	−	+	−
15	+	−	−	−	−	+
16	−	−	−	−	−	−
17	+	+	+	+	+	+
18	+	+	−	−	+	+
19	+	+	+	−	−	+
20	+	+	+	+	−	−
21	−	+	−	+	+	+
22	−	+	+	−	+	+
23	−	+	+	+	−	+
24	−	+	+	+	+	−
25	+	+	−	+	−	+
26	+	+	−	+	+	−
27	+	+	+	−	+	−
28	−	+	+	−	−	−
29	−	+	−	+	−	−
30	−	+	−	−	+	−
31	−	+	−	−	−	+
32	+	+	−	−	−	−

FACTORIAL DESIGN

In order to determine the influence of each variable on the process as well as the effect of the simultaneous change of the variables, a factorial design of experiments was performed. Table I shows a description of the experiments. The range of the independent variables was selected according to the specifi-

TABLE II
Level of the Variables

Variable	Upper level $x(+)$	Lower level $x(-)$
pH (x_1)	3.0	1.0
time (h) (x_2)	3	1
Co(II) concentration (ppm) (x_3)	100	50
Fe(II) concentration (ppm) (x_4)	1000	0
Liquid/chitosan ratio (x_5)	500	50
Na_2SO_4 concentration (mol dm^{-3}) (x_6)	05	0.15

TABLE III
Experimental Results

Expt no.	Cobalt recovery (wt %)	Iron recovery (wt %)	Proton recovery (wt %)
1	0.33	0.39	11.28
2	1.24	3.45	61.72
3	2.36	—	82.05
4	64.63	66.39	99.63
5	1.96	4.88	70.28
6	0.12	—	3.39
7	2.74	4.00	27.39
8	0.28	0.48	2.95
9	2.39	—	24.49
10	0.38	—	14.1
11	3.10	3.58	29.69
12	81.59	—	99.98
13	76.76	69.33	99.88
14	11.19	—	99.80
15	82.28	—	99.9
16	2.80	—	28.88
17	1.27	3.93	76.34
18	1.41	—	80.37
19	86.81	—	99.99
20	85.00	99.87	99.98
21	0.38	0.44	10.67
22	0.38	—	7.53
23	3.32	3.10	24.32
24	0.38	0.40	2.05
25	92.80	97.89	99.91
26	1.28	18.88	61.72
27	6.78	—	99.45
28	3.18	—	34.84
29	2.78	3.78	26.89
30	0.28	—	10.46
31	1.73	—	21.84
32	86.00	—	99.99

cations of the usual cases in hydrometallurgy: acid medium; low concentration of cobalt; high concentration of iron and considerable amounts of sodium sulfate.

The intrinsic variables of the separation process, i.e., contact time, weight of solution/chitosan ratio, were selected according to the results of the literature; the temperature of the process was kept constant at $25 \pm 1°C$. Table II shows the maximum and minimum levels corresponding to each variable, and Table III the results obtained in the experiments, expressed as sorbed metals weight, % Fe and % Co.

RESULTS AND INTERPRETATION

From the results shown in Table III the following information is obtained: the influence of each variable, the first- and second-order interactions between the variables, and the mean value of the response as well as relative meanings.

For this purpose, once the confidence level is established, e.g., 95%, the standard deviation due to the experimental error is related to the second-order influences, and the student parameter t is calculated.

TABLE IV
Significative Influences into a Confidence Range of 95%

Response variable	Input variables
% Fe(II)	L/S
% Co(II)	L/S
% H	$Fe(II)_0$, L/S

TABLE V
Quantitative Linear Relationships

Response variable	Input variables
% Fe(II)	$45.65 + 33.62 X_5$
% Co(II)	$42.7 + 39.27 X_5$
% H	$89.44 + 5.76 X_4 + 10.48 X_5$

In order to discriminate the significance of the influences the following criteria has been applied: If the zero value is out of the confidence range, the variable has been considered to be significant, therefore, the corresponding variable (factor) or interaction of factors has a statistically proved influence.

The obtained results from the statistical analysis are shown in Tables IV and V. From these results it can be concluded that the contact time does not show any appreciable influence on the amount of sorbed cations, indicating that for times after 1 h (1–3 h) there is no quantitative change in the results.

From the graphic representation of the metal retention as a function of the significant variables (Figs. 1–3), a pronounced curvature effect may be ob-
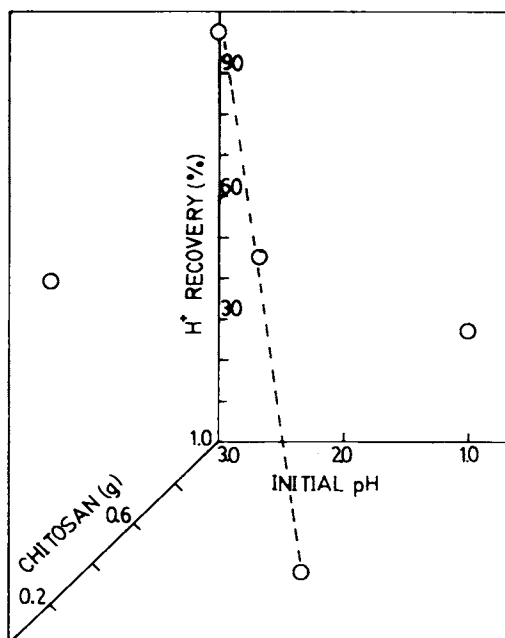

Fig. 1.   Proton sorption as a function of the initial pH and chitosan concentration.
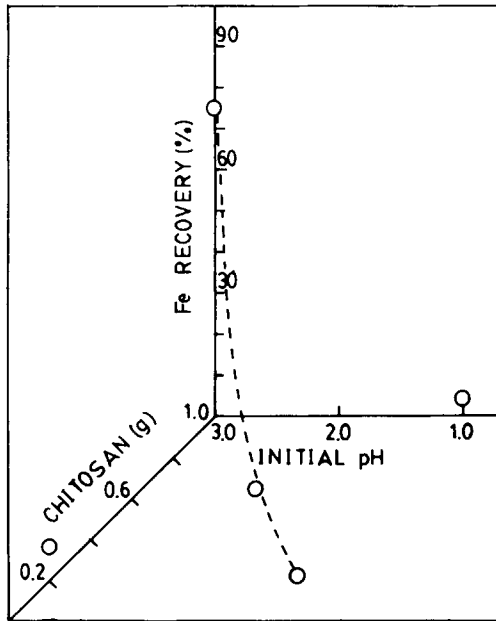
Fig. 2.   Iron sorption as a function of the initial pH and chitosan concentration.
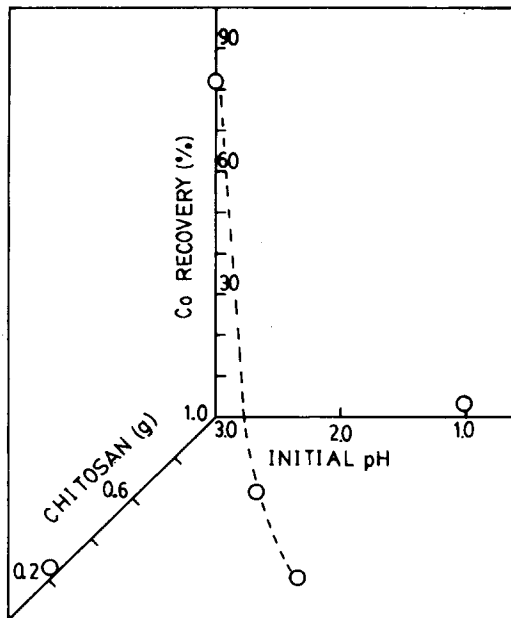

Fig. 3.   Cobalt sorption as a function of the initial pH and chitosan concentration.

served. This effect is mostly due to the important quantitative difference between the results of the retention of metals at pH 1, where the retention is practically negligible and the results at pH 3, where the retention increases considerably. For this reason a different interpretation of the results obtained at pH 1.0 and results at pH 3 is carried out.

Results of the significative influences and linear relationships for the experiments conducted at pH 3.0 are shown in Table IV, where the input variables L/S (weight of solution/weight of chitosan) and initial concentration of iron(II) show a statistical influence on the cation recovery, and in Table V, where a quantitative linear expression has been obtained to relate the response variables, cation recovery wt %, to the input variables after normalization, taking

$$X_i = \frac{x_i - \bar{x}_i}{[x_i(+) - x_i(-)]/2}$$

with $\bar{x}_i$ being the mean value of the input variable i, $x_i(+)$ the upper level of the input variable i, and $x_i(-)$ the lower level of the input variable i in the examined range of variables, which has been shown in Table II.

From these results it can be concluded that for a given value of the initial pH the retention amount of the metals depends basically on the weight of solution per unit of weight of chitosan; the influence of the pH on the retention amount of the cations is studied at constant values of these variables.

pH Influence

To examine the nonlinear influence of this variable on the retention process, a set of experiments performed in the following conditions has been selected:
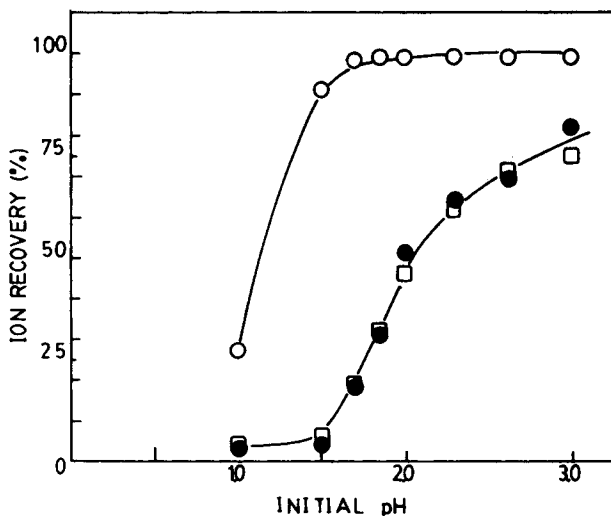

Fig. 4.   Ion recovery, (○) H^+, (□) Fe^{2+}, and (●) Co^{2+}, as a function of the initial pH.

TABLE VI
Sorption of Cations

pH	RH (mmol)	RFe (mmol)	RCo (mmol)
1	27.73	0.65	0.023
1.53	26.69	0.92	0.036
1.77	16.98	3.50	0.151
1.85	14.01	5.90	0.264
2.01	9.86	8.30	0.436
2.32	4.75	11.05	0.543
2.62	2.42	12.72	0.589
2.89	1.29	13.43	0.695

contact time, 1 h; salinity, $0.15M$ initial concentration of Fe(II), 1000 ppm; initial concentration of Co(II), 100 ppm and liquid/solid ratio, 50/1 (50 g solution/1 g chitosan) and the pH range 1.0–3.0. Figure 4 shows the experimental results and Table VI describes the sorbed amount of H^+, Fe^{2+}, and Co^{2+} on the chitosan membrane expressed in mmol; from these results it can be concluded that the retention capacity remains constant and independent of the pH value, being $a_0 = 1.39$ meq/g chitosan, and taking into account that the value II refers to the cobalt and iron valences.

The retention of the protons present in the medium is practically complete, according to Figure 4 for values of the initial pH up to 1.5 and considering that the whole retained amount is constant as has been mentioned above, the retention of the metals can be described by means of their selectivity referred to the fraction of the membrane, which has not been occupied with protons, and, consequently,

$$RH = \frac{V(Co - C)}{m} \quad \text{when } C \to 0$$

$$RH \simeq \frac{V(Co)}{m} \quad \text{being } Co = \left(H_0^+\right)$$

$$S_M = \frac{RM}{1 - RH/a_0}$$

The experimental results obtained in the range of initial pH 1.5–3.0 allow the description of the fraction of the chitosan membrane occupied by metals (RM) by means of the constant selectivity coefficients for iron, $S_{Fe} = 95.5$, and cobalt, $S_{Co} = 4.3$; therefore, the influence of the pH variable on the studied stirred batch system can be successfully described in the investigated range of variables by three parameters a_0, S_{Fe}, and S_{Co}. This kind of semiempirical expressions permits the evaluation of the technical feasibility to use chitosan membranes in the recovery of cobalt from hydrometallurgical solutions containing an important amount of sodium sulfate and iron.

References

1. C. Hanson, *Recent Advances in Liquid–Liquid Extraction*, Pergamon, Oxford, 1971.
2. B. B. Williams, *Ind. Eng. Chem. Fundam.*, 9, 589 (1970).

3. D. O. Hayward and B. M. W. Trapnell, *Chemisorption*, 2nd ed., Butterworths, London, 1964.

4. R. Kunin, *Ion Exchange Resins*, 2nd ed., Wiley, New York, 1958.

5. F. Helfferich, *Ion Exchange*, McGraw-Hill, New York, 1962.

6. K. Dorfner, *Ion Exchangers*: *Properties and Applications*, Ann Arbor Science Publishers, Ann Arbor, MI, 1972.

7. P. Davar and J. P. Wightman, *Adsorption from Aqueous Solutions*, P. H. Tewari, Ed., Plenum Pub, New York, 1981, pp. 163–177.

8. M. V. Kemp and J. P. Wightman, *Virginia J. Sci.*, **32**, 2 (1981).

9. S. Hirano and S. Tokura, Eds. Proceedings of the Second International Conference on Chitin and Chitosan, The Japanese Society of Chitin and Chitosan Sapporo, July, 1982.

10. R. A. A. Muzzarelli and R. Rocchetti, *Anal. Chim. Acta*, **69**, 35–42 (1974).

11. R. Maruca, B. J. Suder, and J. P. Wightman, *J. Appl. Poly. Sci.*, **27**, 4827–4837 (1982).

12. R. A. A. Muzzarelli, *Natural Chelating Polymers*, Pergamon, London, 1973, Chap. 5, pp. 177–220.

13. M. S. Masri and V. G. Randall, Proceedings of the First International Conference on Chitin/Chitosan, R. A. A. Muzzarelli, E. R. Pariser, Eds., MIT Sea Grant, Cambridge, MA, 1978, pp. 277–287.

14. R. A. A. Muzzarelli, *Anal. Chim. Acta*, **54**, 133–142 (1971).

15. R. A. A. Muzzarelli, R. Rocchetti, and G. Marangio, *J. Radioanal. Chem.*, **10**, 17–25 (1972).

16. R. A. A. Muzzarelli and O. Tubertini, *J. Radioanal. Chem.*, **12**, 431–440 (1972).

17. R. A. A. Muzzarelli, *Chitin*, Pergamon, Oxford, 1977, pp. 139–150.

18. R. A. A. Muzzarelli, A. Ferrero, and M. Pizzoli, *Talanta*, **19**, 1222–1226 (1972).

19. R. A. A. Muzzarelli and R. Rocchetti, *Anal. Chim. Acta*, **64**, 371–379 (1973).

20. T. C. Yang and R. R. Zall, *Ind. Eng. Chem., Prod. Res. Dev.*, **23**, 168–172 (1984).

21. R. A. A. Muzzarelli, A. Ferrero Martelli, and O. Tubertini, *Analyst*, **94**, 616–624 (1969).

22. B. J. Suder and J. P. Wightman, *Adsorption from Solution*, R. H. Ottewill, C. H. Rochester, and A. L. Smith, Eds., Academic Press, London 1983, pp. 235–244.

23. R. A. A. Muzzarelli, A. Isolati, and A. Ferrero, *Ion Exchange and Membranes*, *I*, Marcel Dekker, New York, 1974, pp. 193–196.

24. R. A. A. Muzzarelli and R. Rocchetti, *Talanta*, **21**, 1137–1143 (1974).

25. R. A. A. Muzzarelli and R. Rocchetti, *Anal. Chim. Acta*, **70**, 283–289 (1974).