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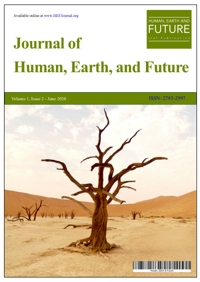

Chemometrics of Solvent Extraction of Mn(II) and Fe(III) Bis(salicylidene) Ethylenediamine Complexes in Acid Medium

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Abstract

In this study, the preparation and solvent extraction parameters of Mn(II) and Fe(III) -bis(salicylidene) ethylenediamine (H_2SAL) were modeled with classical statistical analyses processed using SPSS19.0 software. The linear correlation coefficients for Mn(II) were between 0.59 to 1.0, whereas for Fe(III), it was between 0.48-1.0. The F-values, a measure of the significance of the models, indicated that all the factors are needed, though to differing degrees, for the preparation and extraction of the metal complexes. The significance level for each model was lower than 5%, and as such, the relationship can be generalized to the whole process. The experiments indicated that the solvent extraction combined with the modelling method was accurate, efficient, and reproducible and could be applied on an industrial scale.

Keywords: Modeling; H_2SAL; Solvent Extraction; Metal Ions; SPSS.

1. Introduction

Manganese and iron, the twelfth and fourth most abundant elements in the earth's crust, have concentrations of 9.50×10^2 and 5.63×10^4 respectively [1-2]. Rustamov & Abbasova (2014) [2] have shown that manganese is present in water, sediment, soil and biological samples due to its cumulative nature and, as such, affects adversely the central nervous system. In contrast, iron, on the other hand, has been shown to be important in many biological and biochemical processes, but in excess, toxicity and eventual death of organisms have been implicated [3].

The determination of manganese with complexones from various samples using various analytical methods has been reported, ranging from the use of toluidine [4], mordant brown 33 [5], phenoxazine [6], eosin [7], pyrazolone [8], o-nitrobenzolazosalicylic acid [2] to Schiff bases like bis(salicylidene)ethylenediamine [9]. Similarly, the determination of iron using complexones such as Leucoxylenecyanol, 1,2-dihydroxy-3,4-diketo- cyclobutene(squaric acid), 1,2-2- methy1-3-hydroxy-4-one, Thiocyanate, 9-(4-carboxypheny1)-2,3,7-trihydroxy1-6-Flurone, 2′,3,4′,5,7-Pentahydroxyflavone has been described [10, 11].

In the determination, solvent extraction, where the complexone and the extractant react with the metal ions in the aqueous phase to generate a complex compound that could be retained as aqueous raffinate or transferred into the organic medium, is routinely used. Kandil et al. (2012) and Ogwuegbu & Chileshe (2000) [12, 13] have shown that

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this method leads to favourable issues such as simplicity, selectivity, preconcentration, high speed, high range of determination, accuracy, ease of operation, precision, wide pH or acidity range, thermal stability, and ease of manipulation.

Bis(salicylidene)ethylenediamine -metal complexes have been implicated to be useful in variety of biological, industrial, photochemical, catalytic and other miscellaneous applications [14, 15]. The preparation has always followed the organic synthetic pathways as described by Cozzi [16] without much attention to the solvent extraction method. Similarly, determinations of metal ions in spectrophotometry mainly end in evaluating the spectrophotometric properties such as molar absorptivity, detection limit, and quantification limit without attention to the contributions of the various variables and their level of participation and relevance in complex formation and extraction.

This work models the preparation and extraction conditions of the complexes of Mn(II) and Fe(III) with a Schiff bis base H_2SAL with a view to determining the relevance of the variables and modeling their field applicability.

2. Materials and Methods

Analar grade reagents were used.

Measurement and Characterization

All measurements and characterizations involving FTIR, NMR, UV-Vis, and melting point have been previously reported [17, 18]. A rotary shaker (RF-12 Remi equipment) was used for all equilibrations and shakings. The concentration of the metal ions was determined spectrophotometrically as described elsewhere [19]. The contributions of the various parameters to the preparation and extraction of the metal complexes were done using SPSS19.0 software.

Solution preparation

Solution of hydrochloric acid, H_2SAL, Mn(II) and Fe(II) were prepared according to literature [18].

Synthesis of H_2SAL

Synthesis, characterization and nature of H_2SAL have been reported previously [18, 19].

Metal Extraction Analyses

Preliminary investigation showed highest percentage extraction to be obtained at acid concentration of 10^{-4}M, 0.5% H_2SAL solution, temperature of 30°C and shaking time of 15 min. Solution of metal ions (10 cm^3) was added with 10 cm^3 of 10^{-4} M HCl solution, 5cm^3 of H_2SAL solution and 25 cm^3 of chloroform in a beaker. The mixture was stirred in a magnetic stirrer for 10 min and thereafter shaken for 15 min in a rotary shaker at 300 rpm and 30°C. The solution was then allowed to stand for 10 min in a separatory funnel and the phases separated. The amount of Mn(II) and Fe(III) ions unreacted and in the aqueous phase was determined spectrophotometrically [19]. The quantity of Mn(II) and Fe(III) ions, (b) and extraction efficiency, (%) indicating the quantity of metal ions complexed with H_2SAL is as shown in Equations 1 and 2.

$$b = (x_o - x_e)\frac{Y}{Z} \tag{1}$$

$$Extraction\ efficiency\ (\%) = 100 \times \frac{x_0 - x_e}{x_e} \tag{2}$$

where; x_o= initial amount of Mn(II) and Fe(III) ions,x_e= the equilibrium amount of Mn(II) and Fe(III) ions (mg /mL),Y and Z represents quantity of metal solution and mass of H_2SAL.

3. Results and Discussions

Characterization of H_2SAL

Data on the preparation and characterization of the ligand H_2SAL (Figure 1) has been previously reported [18-21].

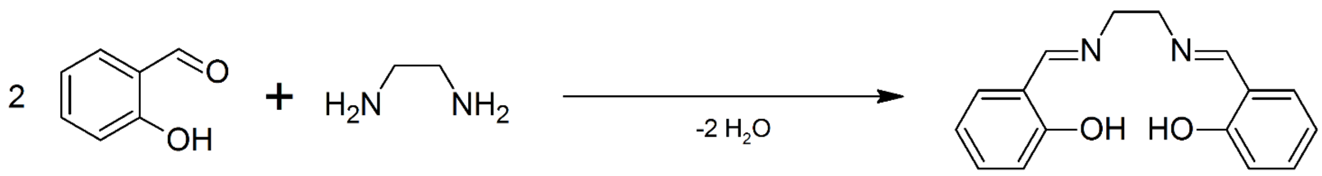

Figure 1. Synthesis of the Schiff base H_2EBNMD

Statistical Consideration

The experimental conditions for the preparation and extraction of Mn(II) and Fe(III) H_2SAL complexes, which include time, acid concentration, ligand concentration, temperature, and metal concentration, were modelled to ascertain the relevance, contribution, and significance of the factors in the process. The results are presented in Tables 1 to 10 as analyzed using statistical and inferential methods.

In Table 1, the coefficient of correlation between the amount extracted and time, temperature, metal concentration, acid concentration, and ligand concentration has multiple R^2 of 0.612, 0.830, 1.000, 0.595, and 0.979, respectively, indicating 51.2, 59.5, and 97.9% variance of the amount extracted to be accurate to time, acid concentration, and ligand concentration.

Table 1. Coefficient of correlation between the variables and amount Mn(II) H_2SAL Complex extracted

Variable	Model	R	R^2	Adj R^2	Std. Error of the estimate	R^2 change	F Change	Df_1	Df_2	Sig f change
Time	1	0.782	0.612	0.482	0.00358	0.612	4.724	1	3	0.118
Temperature	1	0.911	0.830	0.787	0.02299	0.830	19.487	1	4	0.012
Metal conc	1	1.00	1.000	1.000	0.00405	1.000	6606.049	1	2	0.000
Acid conc	1	0.772	0.595	0.514	11.34092	0.595	7.355	1	5	0.042
Ligand conc	1	0.989	0.979	0.968	0.00790	0.979	92.158	1	2	0.011

An examination of Table 2 shows that the F values are significant with ligand concentration having the strongest significant value of 92.158. The F - values show that all the variables, listed have impact on the amount of complex extracted.

Table 2. Results of the ANOVA test for the preparation and extraction of Mn(II) H_2SAL Complex

Variable		Model	Sum of squares	Df	Mean square	F	Sig.
Time	1	Regression	0.000	1	0.000	4.724	0.118
		Residual	0.000	3	0.000		
		Total	0.000	4			
Temperature	2	Regression	0.10	1	0.010	19.487	0.12
		Residual	0.002	4	0.001		
		Total	0.012	5			
Metal conc	3	Regression	0.108	1	0.108	6.606E 3	0.000
		Residual	0.000	2	0.00		
		Total	0.108	3			
Acid conc	4	Regression	946.026	1	946.026	7.355	0.042
		Residual	643.083	5	128.617		
		Total	1589.108	6			
Ligand conc	5	Regression residual	0.006	1	0.006	92.158	0.011
			0.000	2	0.00		
			0.006	3			

Table 3. Result of Regression analysis for the preparation and extraction of Mn(II) H2SAL Complex

Model	Coefficient	Std. err	t	Sig
1a constant	0.066	0.003	24.533	0.000
Time	0.01	0.000	2.174	0.118
1b Constant	0.710	0.032	-4.414	0.012
Temperature	-0.005	0.001		
1c Constant	0.008	0.005	81.2768	0.000
Metal conc	0.029	0.000		
1d Constant	81.320	5.334	-2.712	0.042
Acid conc	016.80	6.154		
le Constant	0.630	0.001	-9.600	0.011
Ligand conc	0.005			

Table 4. Result of Pearson correlation for extraction of Mn(II)H_2SAL complex

Parameters		Amount extracted	Time
Amount extracted	Pearson correlation	1.000	0.782
	Sig (1-tailed)	-	0.059
	N	5	5
Time	Pearson correlation sign (1-Tailed)	0.782	1,000
	Sig (1 – tailed)	0.059	-
	N	5	5
	Pear son correlation	1.00	-0.911
Amount extracted	Sig (1 – tailed)	-	0.006
	N	6	6
	Pearson correlation	-0.911	1.00
Temperature	Fig (1-tailed)	0.006	-
	N	6	6
Amount extracted	Pearson correlation	1.00	1.00
	Sig (1-tailed)	-	4
	N	4	
Metal conc	Pearson correlation	1.00	1.00
	Sig (1-tailed)	0.000	-
	N	4	4
Amount extracted	Pearson correlation	1.00	-0.772
	Sig (1-tailed)	-	0.021
	N	7	7
Acid conc	Pearson correlation	-0.772	1.00
	Sign (1-tailed)	0.021	-
	N	7	7
Amount extracted	Pearson correlation	1.00	0.989
	Sig (1-tailed)	-	0.000
	N	4	4
Ligand conc	Pearson correlation	-0.989	1.00
	Sig (1-tailed)	0.005	-
	N	4	4

From Table 5, the coefficient of correlation between the variables, time, temperature, metal concentration, acid concentration, and ligand concentration, indicates a strong and direct relationship among the variables, with a significance level for each lower than 5%.

Table 5. Coefficient of correlation between the variables and amount of Fe (III) H_2SAL extracted

Variable	Model	R	R^2	Adj R^2	Std. Error of the estimate	R^2 change	F Charge	Df_1	Df_2	Sig f change
Temperature	1	0.817	0.668	0.585	0.10565	0.668	8.045	1	4	0.047
Metal conc	1	1.000	1.000	1.000	0.00063	1.000	2.492ES	1	2	0.00
Time	1	0.754	0.569	0.426	0.01289	0.569	3.963	1	3	0.141
ligand conc	1	0.782	0.612	0.534	15.58787	0.612	7.885	1	5	0.038
Acid conc	1	0.840	0.706	0.633	0.13050	0.706	9.608	1	4	0.036
Time and acid conc	1	0.693	0.480	0.350	1.85794	0.480	3.695	2	8	0.073

Statistical and Inferential Analysis on the Extraction of Fe (III) H_2SAL Complex

An examination of Table 6 shows that the values are significant, with acid concentration having a strong F-value of 9.608. Based on this, it is assumed that the variables temperature, metal concentration, time, acid concentration, and ligand concentration have an impact on the amount of complex prepared and extracted. The regression analysis for generating the possible combination of factors for the preparation and extraction of the complex is shown in Tables 7 and 8.

Table 6. Results of ANOVA Test for preparation and extraction of Fe(1I1) H_2SAL Complex

Source of variation	Model	SS	Df	Ms	F	Sig
Temperature	1. Regression	0.090	1	0.090	8.045	0.047
	Residual	0.045	4	0.011		
	Total	**0.134**	**5**			
Metal conc	2. Regression	0.100	1	0.100	2.492 E 5	0.00
	Residual	0.00	2	0.00		
	Total	0.100	3			
Time	3. Regression	0.000	1	0.000	1.899	0.240
	Residual	0.000	4	0.000		
	Total	**0.000**	**5**			
Acid conc	4. Regression	0.164	1	0.164	9.608	0.036
	Residual	0.068	4	0.17		
	Total	**0.22**	**5**			
Ligand conc	5. Regression	1915.824	1	1915.824	7.885	0.038
	Residual	1214.909	5	242.982		
	Total	**3130.733**	**6**			
Time and acid concentration	6. Regression	25.508	2	12.754	3.695	0.073
	Residual	27.616	8	3.452		
	Total	**53.124**	**10**			

Table 7. The results of regression analysis for the preparation of Fe(III) H_2SAL complex

Model	Coefficient	Std error	T	Sig
a (constant) temperature	0.845	0.145	5.811	0.004
b (constant)	-0.002	0.001	-2.582	0.123
metal conc.	0.028	0.000	499.217	0.000
c (constant)	0.597	0.010	1.430 E 3	0.000
Time	-1.046 E-7	0.001	-1.378	0.240
D (constant)	0.141	0.085	1.659	0.172
Acid	0.526	0.170	3.100	0.036
e. (Constant)	69.534	7.332	9.483	0.000
ligand conc	-23.751	8.458	-2.808	0.38

Table 8. The results of regression analysis for the preparation of Fe(III) H_2SAL complex with metal concentration constant

Model	Coefficient	Std error	t	Sig
1 (constant)	0.832	1.154	0.721	0.492
Acid conc	80.542	32.721	2.461	0.039
Time	0.000	0.000	0.586	0.574

The main model (Equation 4) for extraction of the complex formed from dependent, independent and control variables is a regression model which follows the fixed effect method (Equation 3).

$$Yit = b + ß\ it + Eit \tag{3}$$

The model is of the form $Y = f(x_1, X_2)$ where;

Y = Dependent variable = yit

X_1= First independent variable = acid concentration.

X_2= Second independent variable = time of extraction.

$$Y = 0.832 + 80.532\ x_1,\ i(t_1) + 0.000x_2,\ i(t_{-1}) \tag{4}$$

From Table 9, the relationship among the variables is strong, positive and direct. Also, the significance level for each is lower than 5%, and as such the relation can be generalized to the whole process.

Table 9. Result of Pearson correlation for extraction of Fe(III) H_2SAL complex

Parameters		**Amount extracted**	**Temperature**
Amount extracted	Pearson correlation	1.000	-0.817
	Sig (1-tailed)	6	0.024
	N		6
Temperature	Pearson correlation	-0.817	1.000
	Sig)1-tailed)	0.024	
	N	6	6
Amount extracted	Pearson correlation	1.000	1.000
	Sig (1-tailed)		0.000
	N	4	4
Metal concentrative	Person correlation	1.000	1.000
	Sign (1-tailed)	0.000	
	N	4	4
Amount extracted	Pearson correlation	1.000	-0.567
	Sig (1-tailed)		0.120
	N	6	6
Time	Pearson correlation	-0.567	1.000
	Sig (1-tailed)	0.120	
	N	6	6
Amount extracted	Pearson correlation	1.000	0.840
	Sign (1-tailed)		0.018
	N	6	6
Acid conc	Pearson correlation	0.840	1.000
	Sig (1-tailed)	0.018	
	N	C	6
Amount extracted	Pearson correlation	1.000	-0.782
	Sig (1-tailed)		0.019
	N	7	7
Ligand conc	Pearson correlation	0.782	1.000
	Sig (1-tailed)	0.019	
	N	7	7

In Table 9, the relationship is strong and positive for acid concentration, whereas for time, it is weak. This was also observed in the extraction process where the extraction process is mainly acid concentration dependent and some complexes at certain acid concentrations showed insignificant variation in time of extraction.

4. Conclusion

The preparation and solvent extraction qualities of a Bis-Schiff base have been modeled. The factors of time, acid concentration, temperature, metal ion concentration, and ligand concentration are noted to be significant in complex formation and extraction. The complexation and extraction were suitable for an acid concentration of 0.0001M, shaking time of 15 minutes, a temperature of 30^{o}C, and a ligand concentration of 0.5%. The relationship among these variables was observed to be strong, positive, and direct, with the significance level for each lower than 5%, and as such, the relationship can be generalized to the whole process.

5. Declarations

5.1. Data Availability Statement

The data presented in this study are available in article.

5.2. Funding

The author received no financial support for the research, authorship, and/or publication of this article.

5.3. Institutional Review Board Statement

Not applicable.

5.4. Informed Consent Statement

Not applicable.

5.5. Declaration of Competing Interest

The author declares that there is no conflict of interests regarding the publication of this manuscript. In addition, the ethical issues, including plagiarism, informed consent, misconduct, data fabrication and/or falsification, double publication and/or submission, and redundancies have been completely observed by the author.

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