SIMULTANEOUS SPECTROPHOTOMETRIC DETERMINATION OF Zn^{2+}, Ni^{2+} WITH XYLENOL ORANGE IN SOME INDUSTRIAL WATERS

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ABSTRACT

The formation constants and the concentration of [M] and [ML$_i$] in complex solutions of Ni^{2+} and Zn^{2+} with xylenol orange were determined by spectrophotometric method and principal component analysis. In this way, the spectral data were used to calculate the formation constants of complexes between ions Ni^{2+} and Zn^{2+} with xylenol orange using algorithm of principal component analysis (PCA) in DATAN. The concentration values of Ni^{2+} and Zn^{2+} in synthetic solutions resulting from this technique using xylenol orange (XO) at pH 7.2 agree well with experimental data. This method can be applied to simultaneous determination of Ni^{2+} and Zn^{2+} in the industrial waste waters.

Keywords: *Formation constant, spectrophotometric determination, principal component analysis*

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1. Introduction

In recent years science and technology have been developing, the waste water from urban living areas, residential and industrial zones or mining industries were discharged directly into the water sources. This causes pollution of water. It also caused harm to aquatic organisms and humans. Analysis and monitoring of environmental contaminants have become an important work to contribute to the protection of water resources and to treat the pollution. Environmental contaminants include organic matters and heavy metal ions [1, 2].

Determination of toxic metal ions in wastewaters can be accomplished by different analytical methods, in which the photometric method was considered as a simple method. It is being used widely at many laboratories. However, in practice there are many chemical elements having similar properties. Especially these are not simple for separating and also falsifying the analytical results. Therefore, development of analytical method for simultaneous determination of ions in the wastewater by photometric method is necessary and important for environmental analysis. This would overcome complicate separation techniques, in case of their properties are similar, and UV-Vis spectra of them overlap [3, 4].

This work reports the use of principal component analysis method to estimate formation constants $\log\beta$ of complexes between Zn^{2+} and Ni^{2+} with xylenol orange. The diagrams of species distribution [M], [ML_i] in complex solution were built from the formation constants logβ. This method in turn was used for simultaneous determination of ions Zn^{2+} and Ni^{2+} in synthetic solutions and industrial waste waters using UV-Vis spectra.

2. Experimental method

2.1. Chemicals

Chemicals $NiSO_4.7H_2O$, $ZnSO_4.7H_2O$, $Na_2B_4O_7.10H_2O$, H_2SO_4 and KH_2PO_4 are 99.9% pure. These used for preparing the original and buffer solution. The used ligand xylenol orange is pure.

2.2. Equipment and software

UV-Vis spectra measured by SHIMADU machine connecting 200MHz Pentium computer. UV-Vis spectra were treated by software DATAN 3.1 [6] to determine the formation constants of complexes. Program MS-EXCEL was used to calculate the molecular extinction coefficients at the wavelengths from 500nm to 650nm [8] and to estimate the statistical values. Program Origin 8.0 used to construct chart, plot and UV-Vis spectra [7].

2.3. Determining optimal conditions

Relationship between absorbance at each wavelength and the concentration of ions Zn^{2+} and Ni^{2+} in binary mixtures with xylenol orange can be built by following steps [5]:

- Absorbance maxima of complexes between ions Zn^{2+} and Ni^{2+} and ligand xylenol orange were explored in range 500 nm to 700nm. These maxima were determined at pH 4.2 to 7.4. The formation constants of complexes Zn^{2+}- XO and Ni^{2+}-XO were calculated from experimental UV-Vis spectrum database.

- Determining the limit of quantitative measurements by Beer-Lambert's law.

- Building 25 binary mixtures by Taguchi technique L25(5^2) using concentration levels of Zn^{2+} and Ni^{2+} in solution

Ion	Concentration level, mg/ml				
Ni^{2+}	0.2	0.4	0.6	0.8	1.0
Zn^{2+}	2.0	4.0	6.0	8.0	10.0

- UV-Vis spectra of 25 binary mixtures were measured at pH 7.2 and wavelength range 500nm to 700nm.

- To test this analytical method, 9 binary mixtures were built by alternation of different concentrations for ion Ni^{2+} 0.32, 0.52 and 0.72μg/ml, and ion Zn^{2+} 3.2, 5.2 and 7.2 μg/ml. The UV-Vis spectra also measured at range 500 nm to 700 nm.

2.4. Theoretical method

The relationship of complexes between ions Zn^{2+} and Ni^{2+} with xylenol orange was generated by UV-Vis spectra in wavelength range λ_i(nm) and principal component analysis technique [6]. This can be carried out by program DATAN to determine the formation constants. The nonlinear least square method used was based on the additive nature.

3. Results and discussion

3.1. Exploring condition pH

Complexing ability and absorbance were influenced by different values pH. Therefore the complexes between Ni^{2+} and Zn^{2+} ions and xylenol orange were investigated at pH 4.2 to 7.4. The absorbance changes of complexes are illustrated in Figure 1.

From obtained UV-Vis spectra the absorbance of complexes Ni^{2+}-XO and Zn^{2+}-XO were changed constantly by pH 4.2 to 7.4. But in case of pH 7.0 to 7.4 the absorbance of complexes unchanged and these are stable. So value pH 7.2 can be chosen such as the optimal environmental condition to measure the absorbance of complexes.

On the other hand this can found by checking the statistical values using one-factor analysis of variance ANOVA with factor pH affecting absorbance ABS of the complexes. The factor pH affected greatly absorbance of complex Ni^{2+}-XO (F_{pH} = 59.059 > $F_{0.05}$ = 1.842), and complex Zn^{2+}-XO (F_{pH} = 61.087 > $F_{0.05}$ = 1.842) in range 500nm to 650nm.

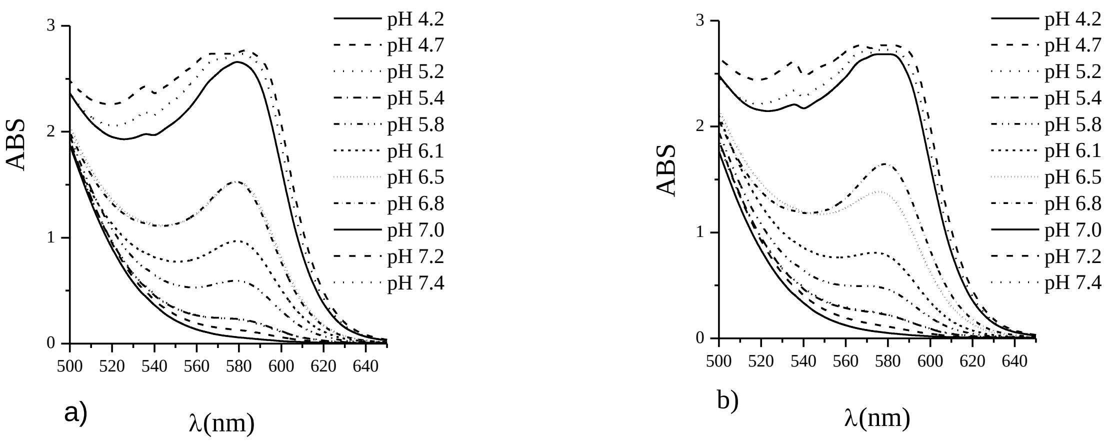


Figure 1: *Absorbance changes ABS of complexes by different values pH: a) Absorbance of complex Ni^{2+}-XO, b) Absorbance of complex Zn^{2+}-XO*

3.2. Determining quantitative limit

Quantitative limit of this photometric method was determined for ions Ni^{2+} and Zn^{2+} with xylenol orange. The influence survey of concentration Ni^{2+} and Zn^{2+} is very important for determining the lowest limit of method using ligand xylenol orange. The quantity of this ligand was kept at concentration 0.0005 mol/lit during the survey. This method allows for determining the concentration of ions Zn^{2+} and Ni^{2+} from 12.0 μg/ml to 52.0 μg/ml and 1.20μg/ml to 5.20μg/ml, respectively, as exhibited in Figure 2. These concentration ranges for ions Zn^{2+} and Ni^{2+} found clear absorbance signal and high reproduction. The concentration limit of ions Ni^{2+} and Zn^{2+} in living waters was within detection and determination limit of this method.

Thus this method can be used to analyze ions Ni^{2+} and Zn^{2+} in water samples assessing the water quality.

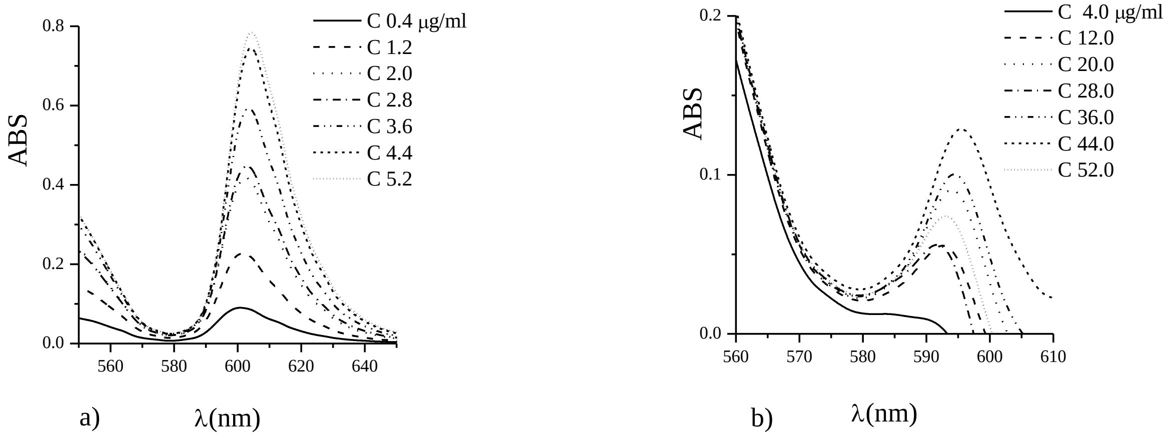


Figure 2: *Absorbance changes in proportion to metal concentration*
a) concentration changes of Ni^{2+}, b) concentration changes of Zn^{2+}

These were also tested by statistical method one-factor analysis of variance ANOVA to evaluate the concentration effect Ni^{2+} and Zn^{2+} for absorbance values of complexes. This can show that the concentration Ni^{2+} displayed great impact for absorbance of complex Ni^{2+}-XO ($F_{Ni} = 11.740 > F_{0.05} = 2.125$) in wavelength range 550nm to 650nm, and the concentration Zn^{2+} also affects for absorbance of complex Zn^{2+}-XO ($F_{Zn} = 2.609 < F_{0.05} = 2.151$) in wavelength range 560nm to 610nm, but it is not greater than ion Ni^{2+}. The concentration ranges of ions Ni^{2+} and Zn^{2+} were determined by Beer-Lambert's law.

3.3. Determining formation constants

The complexes Ni^{2+}-XO and Zn^{2+}-XO were investigated absorbance ability at different values pH 4.2 to 7.4, as shown in Figure 1. From UV-Vis spectra of complexes Ni^{2+}-XO and Zn^{2+}-XO at various values pH the formation constants of them can be calculated by the principal component analysis technique with program DATAN. The data were arranged in three-dimensional matrix:

- Direction 1: wavelength range λ(nm) 500nm to 650nm
- Direction 2: pH range 4.2 to 7.4
- Direction 3: concentration Ni^{2+} $1,7.10^{-5}$M or Zn^{2+} $1,53.10^{-5}$M,

Calculation of formation constants based on the finding principle of the minimum value on sum-of-squared residuals surface (SSR). The finding point on minimization surface would be logβ worth. The logβ values for complexes Ni^{2+}-XO and Zn^{2+}-XO were determined at minimum point on sum-of-squared residuals surface, as exhibited in Figure 3. The iterative number for Ni^{2+}-XO complex is 12, and for complex Zn^{2+}-XO is 10.

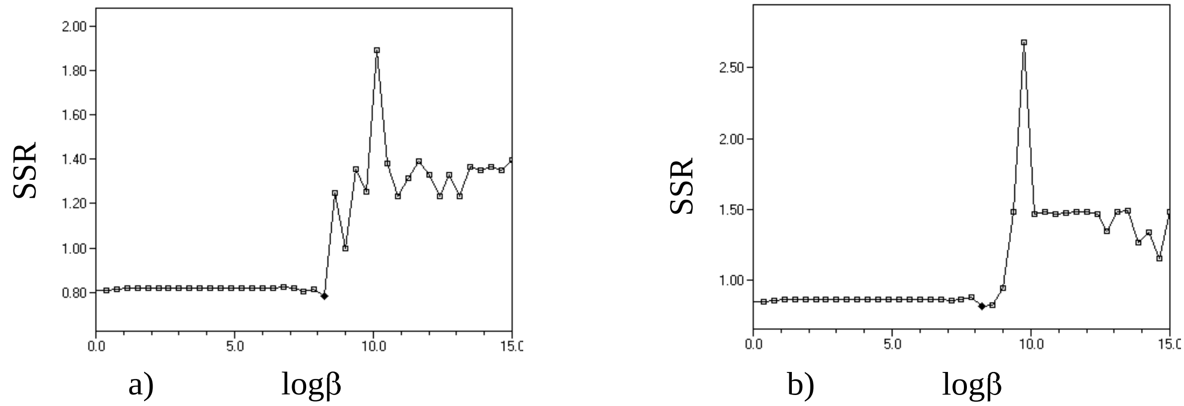


***Figure 3**: Sum-of-squared residuals surface for finding formation constants:*
a) SSR surface of Ni^{2+}-XO complex, b) SSR surface of Zn^{2+}-XO complex

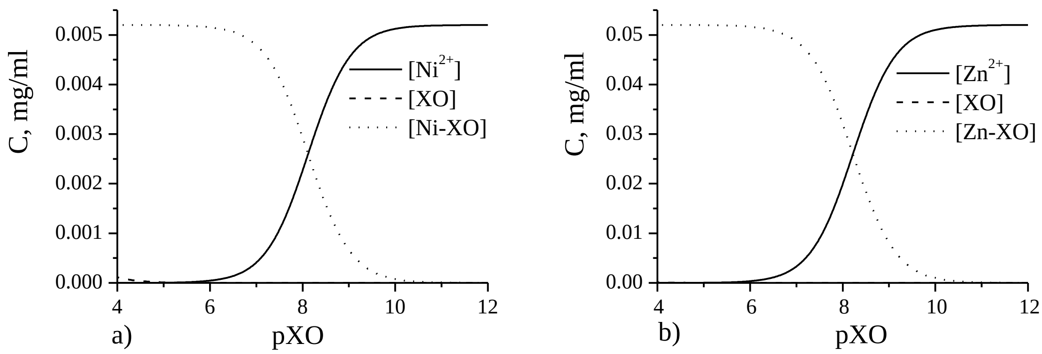


***Figure 4:** Species distribution in the complex solution:*
a) Species distribution of Ni^{2+}-XO, b) Species distribution of Zn^{2+}-XO

From sum-of-squared residuals surface the formation constant logβ of for Ni^{2+}-XO complex at values pH 4.2 to 7.4 is 8.12, and for Zn^{2+}-XO complex the formation constant logβ is 8.25 was calculated at pH range 4.2 to 7.4. This value is close to value logβ = 6.146 of complex Zn^{2+}-XO resulting from pH 5.8 to 6.2 [1]. From the formation constants of complexes Ni^{2+}-XO and Zn^{2+}-XO the diagram of species distribution can be built for concentration changes of components in solution, as depicted in Figure 4.

3.4. Determining molar absorptivity coefficient ε

The use of spectrophotometric analysis method for metal ions in waste water samples based on the principle of color complexing between metal ions Ni^{2+}, Zn^{2+} and xylenol orange. In this case UV-Vis spectra of them are overlapped in range 500nm to 600nm, so molar absorptivity coefficients ε need to be calculated at all wavelengths.

These are based on the additive nature of Beer-Lambert's law combining nonlinear least square method. Computational process implemented by steps:

- The values of molar absorptivity ε are relied on UV-Vis spectra of pure standard ions Ni^{2+}, Zn^{2+} and xylenol orange.
- The value of molar absorptivity ε are calculated relying on binary mixtures, in which two ions Ni^{2+}, Zn^{2+} present simultaneously with xylenol orange.

- Molar absorptivity coefficients (are tested by comparison of value (obtained from two techniques above. This is the important basis to predict the concentration of ions in environmental samples.

Molar absorptivity coefficients (resulting from techniques are exhibited in Figure 5.

Figure 5: a) Comparison of molar absorptivity coefficient (of Ni2+-XO and Zn2+-XO;
b) Experimental and calculated absorbance derived from molar absorptivity ε

Molar absorptivity coefficients ε were calculated by two techniques above using the nonlinear least squares method for single and mixed solutions of two ions Ni^{2+} and Zn^{2+}. Those showed in good fit each other and the effect of them is negligible although the concentration Zn^{2+} is 10 times of concentration Ni^{2+}.

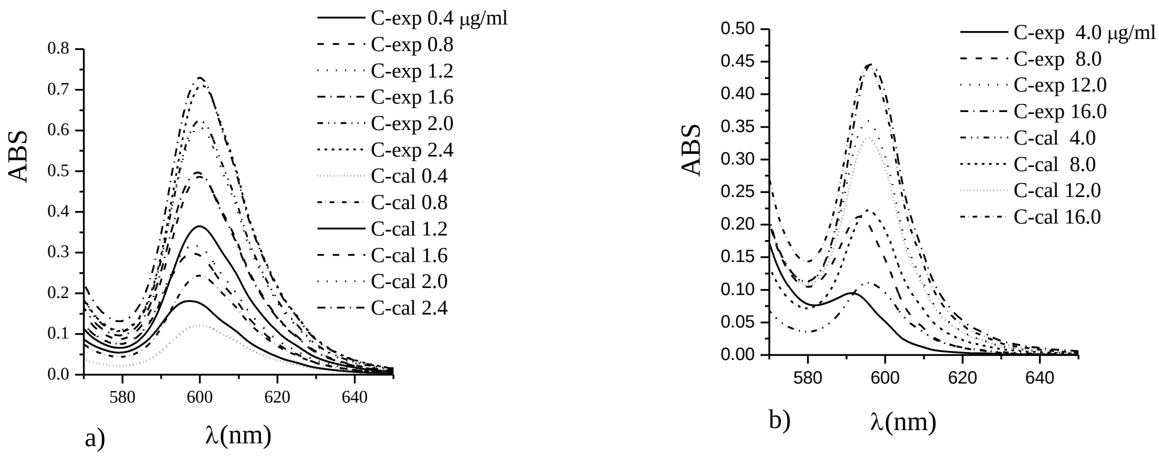


Figure 6: *a) Experimental and calculated absorbance of complex Ni^{2+}-XO;*
b) Experimental and calculated absorbance of complex Zn^{2+}-XO

The molar absorptivity coefficient values ε can be used to calculate the absorbance of complex solution Ni^{2+}-XO, while change of Ni^{2+} concentration 0.4μg/ml to 2.4μg/ml. Similarly, for Zn^{2+}-XO complex solution the Zn^{2+} concentration changes from 4.0μg/ml to 16.0μg/ml. The calculated absorbance was compared with the experimental absorbance of complexes, respectively, as depicted in Figure 6. The result shows that the concentration Ni^{2+} resulting from this method is in very good agreement with experimental data at the smallest critical level of 1.2μg/ml; for ion Zn^{2+} this methods can be also determined at the lowest quantitative limit 8.0μg/ml.

3.5. Building binary mixtures

Concentrations of Ni^{2+} and Zn^{2+} ions should be selected in linear range of Beer-Lambert's law, but the concentration limits for these ions are in qualification limit range of waste water. Matrix of 25 binary solutions was constructed by Taguchi technique L25(5^2), as given in Table 1. The 25 UV-Vis mixed spectra obtained from experimental measurement were used to determine the molar absorptivity coefficients ε and then these in turn were used to determine the concentration of Ni^{2+} and Zn^{2+} in 9 synthetic samples, as shown in Table 2. The predicted results were compared with experimental values.

The ARE value, % is calculated by formula

$$\text{ARE, \%} = \frac{\left|C_{Me,exp} - C_{Me,cal}\right|}{\left|C_{Me,exp}\right|}.100 \qquad (1)$$

The average error of global GAME, % is determined by formula

$$\text{GAME, \%} = \frac{100}{n}\sum_{i=1}^{n}\left|(C_{Me,exp})_i - (C_{Me,cal})_i\right| / (C_{Me,exp})_i \qquad (2)$$

Here, $C_{Me,exp}$, $C_{Me,cal}$ is concentration of ions in the mixture *i*.

Table 1: *Mixtures of Ni^{2+} and Zn^{2+} ions at 5 concentration levels using Taguchi technique*

Mix	Experimental values		Calculated values		ARE, %	
	Ni^{2+}(mg/ml)	Zn^{2+}(mg/ml)	Ni^{2+}(mg/ml)	Zn^{2+}(mg/ml)	Ni^{2+}	Zn^{2+}
1	0.20	2.0	0.188	2.144	5.788	7.184
2	0.20	4.0	0.224	3.974	12.183	0.641
3	0.20	6.0	0.194	6.002	3.231	0.039
4	0.20	8.0	0.173	7.639	13.268	4.513
5	0.20	10.0	0.179	9.747	10.312	2.531
6	0.40	2.0	0.392	1.853	2.106	7.326
7	0.40	4.0	0.337	4.366	15.855	9.146
8	0.40	6.0	0.397	5.631	0.666	6.149
9	0.40	8.0	0.443	8.354	10.634	4.420
10	0.40	10.0	0.388	9.950	2.886	0.504
11	0.60	2.0	0.570	2.024	4.996	1.218
12	0.60	4.0	0.533	4.679	11.244	16.970
13	0.60	6.0	0.635	6.526	5.789	8.761
14	0.60	8.0	0.598	7.735	0.258	3.315
15	0.60	10.0	0.570	9.744	4.949	2.563
16	0.80	2.0	0.776	1.855	3.047	7.261
17	0.80	4.0	0.776	4.245	3.018	6.137
18	0.80	6.0	0.763	5.846	4.564	2.569
19	0.80	8.0	0.781	7.547	2.365	5.667
20	0.80	10.0	0.801	9.902	0.118	0.983
21	1.00	2.0	0.995	2.245	0.466	12.233
22	1.00	4.0	0.746	3.846	25.422	3.854
23	1.00	6.0	0.955	5.965	4.513	0.589

24	1.00	8.0	1.357	7.557	35.679	5.541
25	1.00	10.0	1.002	9.893	0.237	1.065

Values GAME, % = 7.344% for Ni^{2+}; GAME, % = 4.847% for Zn^{2+} obtained from the calculation errors ARE, % in Table 1. With calculated errors this showed that the method can be applied to predict the concentration of ions from molar absorptivity coefficients ε and UV-Vis experimental spectra. The obtained results are acceptable and reliable. These are in uncertain range of experimental measurements.

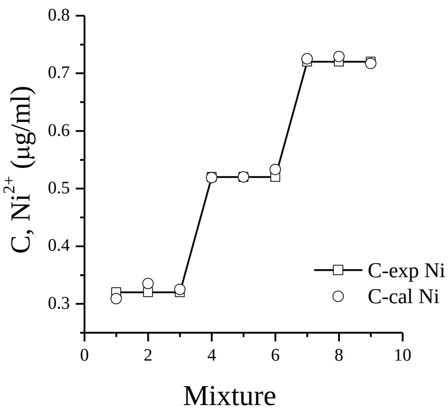
From the determination results of molar absorptivity coefficients ε of complexes Ni^{2+}-XO and Zn^{2+}-XO, these in turn, were carried out to test by 9 different concentration mixtures of Ni^{2+} and Zn^{2+}, as given in Table 2.

From analysis results for nine synthetic samples, the testing error results GAME, and % are small for concentrations of Ni^{2+} and Zn^{2+} ions. These proved that difference between calculated and experimental values are not significant. The initial results obtained from this method showed that analytical results here are consistent with the actual values, can be seen on Figure 7.

Table 2: *The 9 binary mixtures of Ni^{2+} and Zn^{2+} ions for inspection.*

Mix	Experimental values		Calculated values		ARE, %	
	Ni^{2+}(mg/ml)	Zn^{2+}(mg/ml)	Ni^{2+}(mg/ml)	Zn^{2+}(mg/ml)	Ni^{2+}	Zn^{2+}
1	0.32	3.2	0.309	3.225	3.329	0.770
2	0.32	5.2	0.335	5.244	4.543	0.840
3	0.32	7.2	0.325	7.257	1.411	0.798
4	0.52	3.2	0.519	3.225	0.261	0.796
5	0.52	5.2	0.520	5.200	0.010	0.007
6	0.52	7.2	0.533	7.190	2.438	0.144
7	0.72	3.2	0.725	3.231	0.761	0.976
8	0.72	5.2	0.729	5.255	1.215	1.053
9	0.72	7.2	0.717	7.387	0.353	2.594

GAME value, % = 1.591% for Ni^{2+}; GAME, % = 0.886% for Zn^{2+}. These results obtained from the calculated errors ARE, % Table 2.



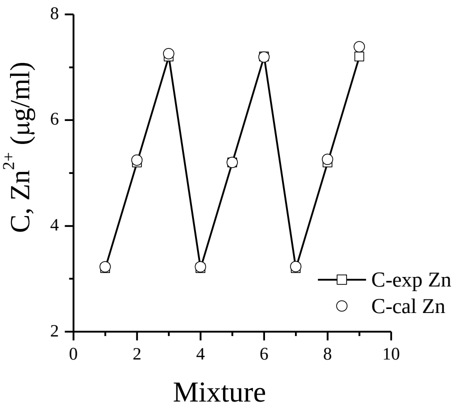


Figure 7: *a) Comparison of experimental and calculated concentration Ni^{2+}.*
b) Comparison of experimental and calculated concentration Zn^{2+}.

4. Conclusion

This work includes initial results of complexing exploration process between Ni^{2+} and Zn^{2+} with xylenol orange at different conditions pH. The formation constant values of complexes Ni^{2+}-XO and Zn^{2+}-XO were determined by UV-Vis spectral data at pH 7.2. The formation constant logβ of complex Zn^{2+}-XO was close to constant value logβ of Zn^{2+}-XO, which it was determined at pH 5.8 to 6.2 [1]. The diagram of species distribution of complexes in solution was built by formation constant values. From the complexing process of Ni^{2+} and Zn^{2+} with xylenol orange, these can be developed to determine simultaneously the concentrations of Ni^{2+} and Zn^{2+} in water samples. The molar absorptivity coefficients were determined from UV-Vis spectra of single ions and ion-mixture solutions. These were used to predict the concentrations of Ni^{2+} and Zn^{2+} ions. The global errors are small. The predicted concentrations of Ni^{2+} and Zn^{2+} were not significantly different from actual value. This method shows that initial deployment can be used to determine the concentration of Ni^{2+} and Zn^{2+} ions in actual samples.

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XÁC ĐỊNH TRẮC QUANG ĐỒNG THỜI Zn^{2+}, Ni^{2+} BẰNG XYLENOL DA CAM TRONG MỘT VÀI MẪU NƯỚC CÔNG NGHIỆP

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TÓM TẮT

Các hằng số tạo thành và nồng độ của [M] và [ML_i] trong dung dịch phức của Ni^{2+} và Zn^{2+} với xylenol da cam được xác định bằng phương pháp trắc quang và phân tích thành phần chính. Trong phương pháp này, dữ liệu phổ được sử dụng để tính toán các hằng số tạo thành của các phức giữa Ni^{2+} và Zn^{2+} với xylenol da cam sử dụng giải thuật phân tích thành phần chính (PCA) trong DATAN. Các giá trị nồng độ ion Ni^{2+} và Zn^{2+} trong các dung dịch tổng hợp được xác định bằng phương pháp này ở pH = 7,2 sử dụng xylenol da cam phù hợp tốt với dữ liệu thực nghiệm. Phương pháp này có thể áp dụng để xác định đồng thời Ni^{2+} và Zn^{2+} trong mẫu nước thải công nghiệp.

Từ khóa: *hằng số tạo thành, xác định trắc quang, phân tích thành phần chính*

REFERENCES

[1]. S. Karel, J. Ivan, *The photometric determination of zinc with xylenol orange,* Talanta, Vol. 8, P. 203-208, (1961).

[2]. K. L. Cheng, *Analytical applications of xylenol orange-III: Spectrophotometric study on the hafnium-xylenol orange complex,* Talanta, Vol. 3, Issue 1, P. 81-90, (1959).

[3]. K. Ogura, S. Kurakami, K. Seneo, *Electroanalytical and spectroscopic studies on metal complexes with sulphonephthalein derivatives-II: Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) complexes with xylenol orange,* J. Inorganic and Nuclear Chemistry, Vol.43, Issue 6, P. 1243-124, (1981).

[4]. A. K. Mukherji, *Simultaneous spectrophotometric determination of thorium and the rare earths with xylenol Orange,* Microchemical J., Vol. 11, Issue 2, P. 243-254, (1966).

[5]. T. Madrakian, R. Moeina, M. Bahramb, *Simultaneous Spectrophotometric Determination of Zinc and Nickel in Water Samples by Mean Centering of Ratio Kinetic Profiles,* J. Chinese Chemical Society, Vol. 55, P. 788-793, (2008).

[6]. *MultiD Analyses AB DATAN for Chemical Analysis,* Users manual, V3.1, (2006).

[7]. *OriginLab corporation, Northampton, MA 01060,* Users manual, OriginPro v7.0, (2003).

[8]. *Microsoft office corporation EXCEL 2003,* Users manual (2003).