

Cobalt and Nickel Separation in Hydrometallurgy using Clinoptilolite as Ion- Exchanger

Banza Musamba*, John Kabuba and Hilary Rutto

Abstract—Cobalt and nickel have similar physical and chemical properties that makes their separation a serious problem in hydrometallurgy. In this work, modified clinoptilolite as ion exchanger has been identify for selective separation of cobalt from nickel. The characterization of clinoptilolites before and after modification was done using Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and X-ray diffraction (XRD). The results showed that the separation of cobalt from nickel strongly depend on pH, initial concentration, mass of the adsorbent, particle sizes and temperature. High separation was obtained under following conditions pH 6, initial concentration 600 mg/L, mass of the adsorbent 10 g, particle sizes 1mm and temperature 25°C. The equilibrium sorption isotherms were analyzed by the Langmuir and Freundlich. The results showed that Langmuir isotherm describes better the adsorption process. The pseudo-first and second order model were used in analyzing kinetic data, absorption kinetics obeyed the second Pseudo order model that indicate that the rate limiting step for the process involves chemical reaction. Thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated and negative results revealed that the process was spontaneous and exothermic.

Keywords—Clinoptilolites, modification, ion exchanger, cobalt and nickel separation, hydrometallurgy.

I. INTRODUCTION

The hydrometallurgical industry produces many types of streams, increasing cost and required more effective method for cleaning these wastes. The recovery of heavy metals from the hydrometallurgical effluent stream it is very important. The effective recovery of these metals is possible only if the separation process is selective enough [1].

Cobalt can be used in alloys for airplane engine parts (corrosion resistant), electroplating, batteries, stainless steel and to treat cancer and anaemia because cobalt stimulates the red blood cells production. Nickel can be used in the manufactured of coins, stainless steel, corrosion resistant alloys such as

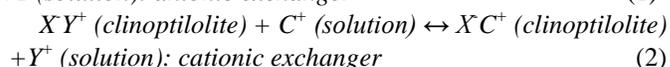
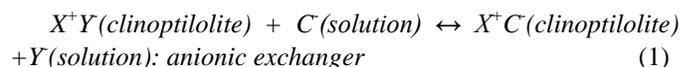
(Monel, Inconel and Invar), nickel-cadmium batteries and treatment of sea water into fresh water at the desalination plant [2].

Cobalt and nickel are inseparable in aqueous solution. Their position in the periodic table as transition metal result in similar chemical performance and therefore their separation becomes difficult. In aqueous dilute solution nickel and cobalt exist as Ni^{2+} and Co^{2+} hexahydrated; the rate exchange of water on nickel is very lower than cobalt. The complex ion formation proceeds much easily with Co^{2+} than Ni^{2+} [3].

Several methods have been used for the separation processes. Most of them are physico- chemical processes and these include precipitative, separation method using resins ion exchanger, solvent extraction and pressure hydrogen [4]. In general, these methods have been found to be only partially and not economically feasible for the separation of cobalt and nickel [5].

This project has identified the high potential of clinoptilolite in separating cobalt and nickel from hydrometallurgical industrial wastewater stream due to their high ion exchange abilities, simple operation, minimal waste generation, low costs and availability. Clinoptilolites could be used on a large scale as ion exchanger for heavy metals from industrial effluent. It can be modified and regenerated. The metal ions adsorbed by the clinoptilolites can be recovered and used industrially for several applications [6; 7].

The ion exchange is defined as the reversible exchange of ions between two or more phases, one of which is liquid phase and solid phase. The ion exchanger is not soluble in the medium in which the process is taking place. Ion exchanges processes are rapid and follow the reaction in the Eq. (1) and (2), however the kinetics of reaction become uncontrollable and difficult in heterogeneous systems. The two reactions show the ion exchange between the ion in solution and the clinoptilolites [8].



Clinoptilolite is one of the most abundant forms of zeolite that is found naturally on earth. It is stable at high temperature [9] gave the typical formula for the clinoptilolite as $M_{2/n}O.Al_2O_3.xSi_2.yH_2O$. The atomic structure of clinoptilolite is

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based on three-dimensional frameworks of silica and alumina tetrahedra. Clinoptilolites is inorganic with a strong attraction for cations of transition metals series in the periodic table. The ion exchange property of clinoptilolites has been attributed to its aluminosilicate structure. Isomorphous replacement of Al with Si in the structure results in negative charge [10]. This negative charge is stabilized by alkaline earth cations of Ca^{2+} , K^+ , Na^{2+} and Mg^{2+} in the zeolite [11].

II. EXPERIMENTAL

A. Materials and Solution

The clinoptilolite used in this study was supplied by Pratley Mining Company south Africa. The clinoptilolite was first washed in distilled water to remove fines and impurities and dried in the oven at 60 °C for 48 hours. Clinoptilolites particles was crushed and screened through a range of sieves, only particles from 1000- 2500 μm were used in the study. The sieves were shaken for 10 minutes and for Clinoptilolites characterization 75 μm particles was used. The powder was then characterized using an XRD (Phillips X'pert Model 0993), XRF (Phillips Magix Pro), FTIR (Varian 7000) and SEM (Philips XL 30FEG) before and after clinoptilolites modification.

The synthetic solution was prepared using cobalt chloride hexahydrated and nickel chloride hexahydrated. Hydrochloric acid and sodium hydroxide was used to adjust the pH. The modification of clinoptilolites was done using NaOH, Ethylenediaminetetraacetic acid (EDTA) and succinic acid. All the chemicals used were analytical grade reagents from sigma Aldrich. The clinoptilolite was modified by contacting them to 2M of NaOH for 48 hours and 2M EDTA for 72hour at 25°C Then dried at 60°C for 24 hours. Lastly, modified clinoptilolites contacting with succinic acid for 72 hours then dried at 50°C temperature.

B. Experimental Procedure

The ion exchange process on the clinoptilolite was performed in a thermostatic shaker at 180 rpm. A mass of clinoptilolites 2 to 10g was contacted in conical flask with 110 ml solution that contains Cobalt and Nickel cations. The metal ion concentration 50 to 500 mg/L, the particles size 1000 to 2500 μm and temperature 25 to 55°C. The pH values were adjusted from 3 to 9. Every hour for a 5-hour period, 10 ml of the suspension was taken and filtered from the mixture and tested for ion concentration using the atomic adsorption spectrophotometer (AAS). The experiment was left to run for a period of 24 hours to determine the equilibrium concentrations.

The performance of the clinoptilolite at exchanging heavy metals in the solution was assessed by calculating the percentage.

The Equation (3) will be used for the heavy metals removed

$$\% = \frac{(C_a - C_b)}{C_a} \times 100 \quad (3)$$

where C_a and C_b are the initial ion concentration and final ion concentration of the solution, respectively.

The mass of removal metal ion per gram of the solvent was calculated by the Eq. (4):

$$q_e = \frac{(C_a - C_b)}{M} \times V \quad (4)$$

where V and M are the volume of solution (mL) and amount of sorbent (g), respectively.

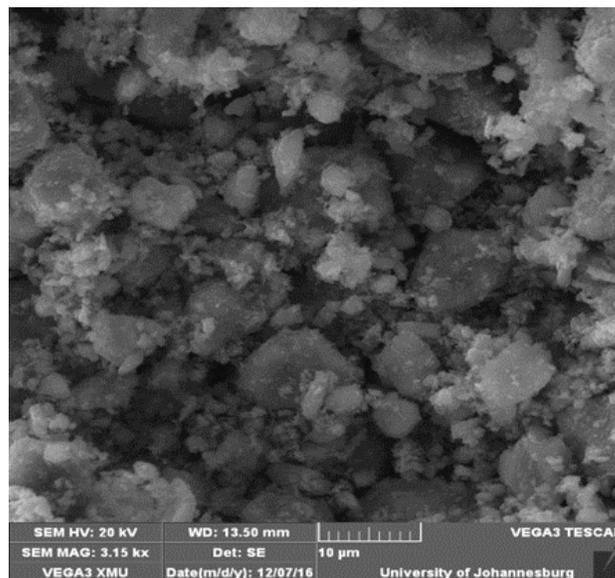
III. RESULTS AND DISCUSSION

A. X-Ray Fluorescence (XRF)

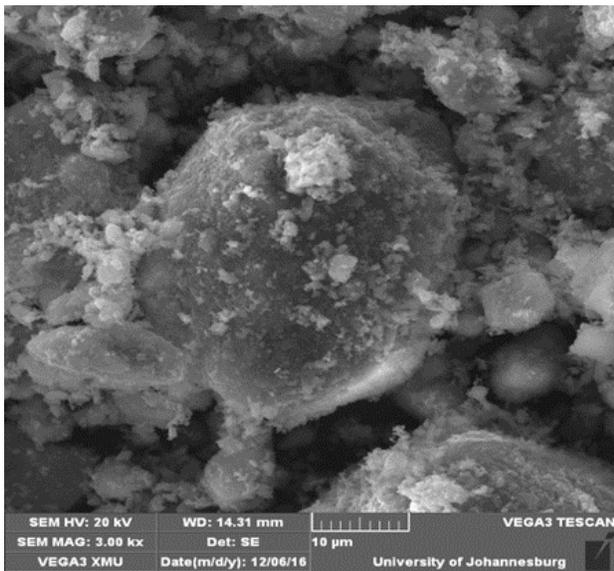
XRF analysis showed that clinoptilolites was silico based zeolites when taking in account the major component which was SiO_2 for both natural and modified clinoptilolites. The elemental composition results revealed that the composition of amorphous SiO_2 in the natural clinoptilolites was 65.54 and 67.78 after modification. The ratio of $(\text{Na}+\text{K})/\text{Ca}$ was 3.93 and 3.33 for natural and modified clinoptilolites respectively. The increase of the ratio after modification is the result of EDTA [12]. And effect of succinic acid in clinoptilolite [13]. It can be seen that the crystallinity of clinoptilolites is affected by the modification.

B. Scanning Electron Microscope (SEM)

SEM image of natural and modified at the same magnification were presented in Fig. 1. The SEM image of modified clinoptilolite (B) shows a typical morphology of sedimentary. For both natural and modified cavities of different shapes and sizes could be observed. The natural clinoptilolite indicates the presence of small globular particles and modified shows bigger and irregular sizes [14]. This can be attributed to the fact that modification is a surface phenomenon and EDTA and succinic acid chemically modifies the clinoptilolite.



(A)



(B)

Fig. 1. SEM images for natural clinoptilolite (A) and modified clinoptilolite (B)

C. X-Ray Diffraction (XRD)

The XRD pattern of clinoptilolite was illustrated in Fig. 2 for natural clinoptilolite. Natural clinoptilolites was found to be monoclinic, crystalline and heulandite with highest peak occurring at 2θ value of 25. The modified clinoptilolite in Fig. 3 has also monoclinic crystallography too with highest crystalline peak appearing at 2θ value of 10. Most of peaks occurring between 10- 40.

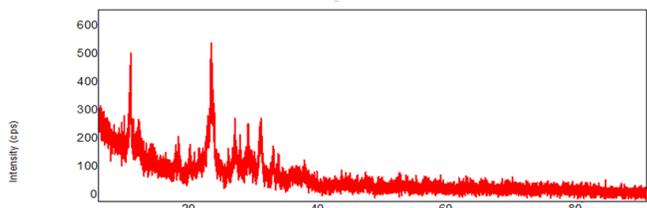


Fig. 2. XRD patterns for natural clinoptilolite

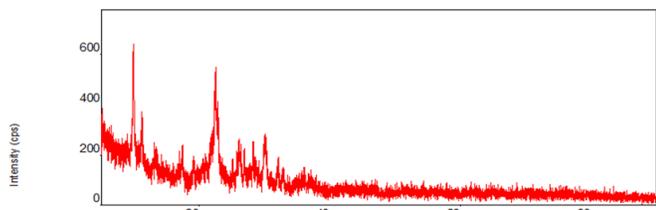


Fig. 3. XRD patterns for natural clinoptilolite

D. Fourier Transform Infrared Spectroscopy (FTIR)

Peaks positions were observed at 3413, 1632, 1020 and 792 cm^{-1} in Fig. 4 and peaks 3415, 2925, 2856, 1635, 1022 and 788 cm^{-1} in Fig. 5. Bands connected with Si-O(Al) and Si-O(Si) vibrations in tetraedra or alumino and silicon oxygen (range of 1100 to 450 cm^{-1}). Bands due to the presence of zeolitic water (range 1700 to 3800 cm^{-1}) and bands due to the lattice vibration of structural unit (650- 750 cm^{-1}). Bands due to C=C and C-O stretching vibration (range 1100 to 2900 cm^{-1}). The position of

the main band at 1029 cm^{-1} shift to 1022 cm^{-1} is due to the stretching vibration of Si-O(Al) and Si-O(Si).

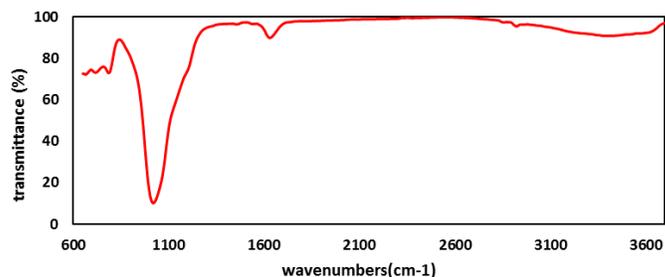


Fig. 4. FTIR patterns of natural clinoptilolite

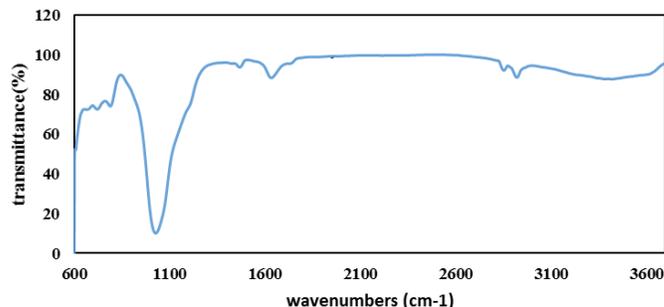


Fig. 4. FTIR patterns of modified clinoptilolite

E. Effect of pH

The effect of pH on the metals removal by modified clinoptilolites was studied in the range of 2 to 9 and keeping another parameters constant [14]. The influence of pH on cobalt and nickel separation was illustrated in Fig. 6. The removal efficiency of cobalt and nickel increase with an increase of pH from 3 to 6. The maximum removal efficiency for cobalt and nickel was 97% and 36% respectively. This is due to electrostatic force between the negatively charge of the modified clinoptilolites and positives charge of metals. Stronger acidic pHs protons present in the solution compete with cobalt cations compare to nickel cations for sites available of the modified clinoptilolites which gave a good separation between nickel and cobalt. Decrease in removal efficiency of cobalt 87% and nickel 27% at pH 9 is due to occupation of sites available of the modified clinoptilolite [14].

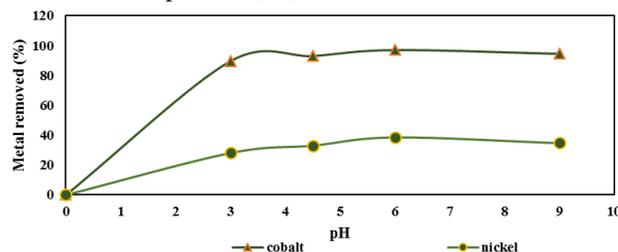


Fig. 6. Effect of pH on the removal of cobalt and nickel onto modified clinoptilolites

F. Effect of Mass of Adsorbent

The Adsorbent dosage is an important parameter in the ion exchange process because is influencing the capacity of modified clinoptilolites for a given initial concentration. In this

study, the clinoptilolite dosage was varied from 2g to 10g. Co²⁺ ions were removed from the aqueous solution at small the dosage of modified clinoptilolites. When the dosage of modified clinoptilolites was increased from 2 to 10g the removal percentage increases from 78% to 98% for cobalt and 16% to 37% for nickel. The percentage removal of cobalt and nickel increases with the increase of modified clinoptilolites dosage is due to the to the increase in active site on the modified clinoptilolites making the penetration of cobalt ions easy compare to nickel. The highest removal efficiency was obtained at 10g with 98% of cobalt. For further experiment the amount of clinoptilolites was selected as 10g.

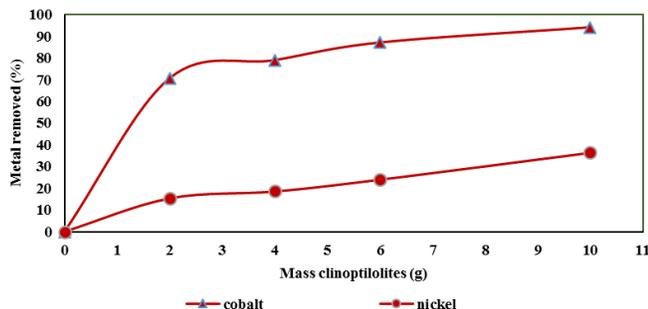


Fig. 7. Effect of mass of clinoptilolites on the removal of cobalt and nickel onto modified clinoptilolites

G. Effect of Particles Size

The effect of pH on the metals removal by modified clinoptilolites was studied in the range of 1000µm to 2500 µm and keeping another parameters constant. The influence of particles size on cobalt and nickel separation was illustrated in Fig. 8. The removal efficiency of cobalt and nickel decreases with an increase of particles sizes. At 1000 µm the percentage removal of cobalt was 95% and nickel 34% then decrease to 85% for cobalt and 21% for nickel at 2500 µm. The increase in efficiency of removal for cobalt is due to the increase in external surface area of the small particles size of the modified clinoptilolites. The maximum removal efficiency for cobalt and nickel was 95% and 34% respectively for 1000µm.

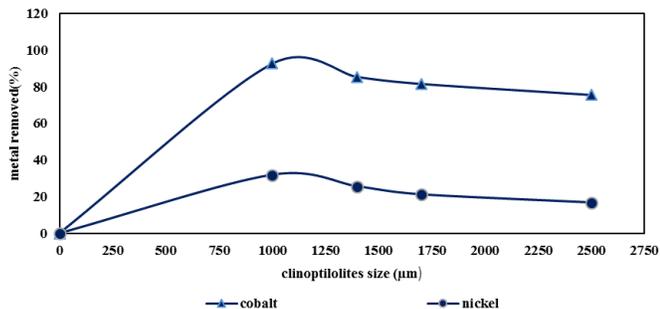


Fig. 8. Effect of clinoptilolites sizes on the removal of cobalt and nickel onto modified clinoptilolites

H. Effect of ion Concentration

The effect of initial concentration for cobalt and nickel removal from aqueous solution by modified clinoptilolites was determine. The cobalt removal efficiency increase from 77% to 97% and nickel from 20% to 35% in the initial concentration from 50mg/L to 600 mg/L due to the equilibrium nature of

Co-clinoptilolites modified and ion exchange process [15]. then decrease to 90% for cobalt and 31% for nickel at 900 mg/L this reduction may be resulted from saturation of the modified clinoptilolites surface.

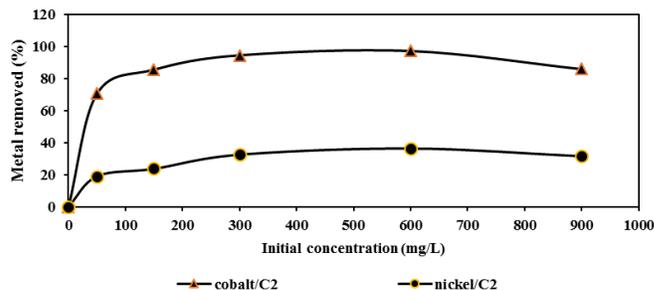


Fig. 9. Effect of initial concentration on the removal of cobalt and nickel onto modified clinoptilolites

I. Effect of Temperature

Temperature is an important parameter for the removal of heavy ions metal in the solution. Because temperature of the of the solution can affect the solution/solid interface. The effect of temperature was studied in a range of 25°C to 55°C and the remaining particle were kept constant. The removal efficiency decrease with an increase in temperature and good separation of cobalt from nickel was illustrated in fig. cobalt removal percentage decreased from 96% to 85% and nickel decreased from 37% to 21% as shown in Fig. 10. Is due to the mobility and competition of cobalt and nickel ions onto modified clinoptilolites [12; 14]. The maximum temperature was found to be 25°C with 96% of cobalt and 37% of nickel percentage recovery.

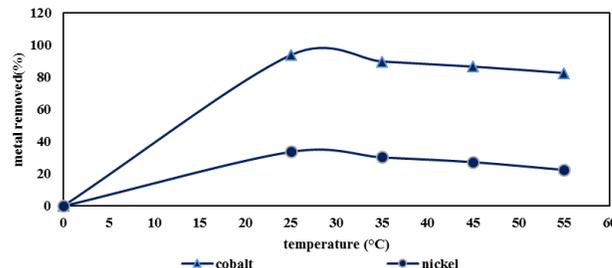


Fig. 10. Effect of temperature on the removal of cobalt and nickel onto modified clinoptilolites

J. Effect of Adsorption Isotherm

Adsorption isotherm explains the relationship between the amounts of cobalt and nickel ions adsorbed onto modified clinoptilolites for the design of the process.

- Langmuir isotherm (see Eq. 5)

$$q_e = \frac{q_m K_L C_t}{1 + K_L C_t} \tag{5}$$

where C_t equilibrium metal concentration, q_L adsorption capacity maximum (mg.g⁻¹), K_L Langmuir constant (L.mg⁻¹) and q_t is the amount of metal ion adsorbed at equilibrium (mg.g⁻¹) at a given temperature.

- Freundlich isotherm (see Eq. 6)

$$q_e = K_F C_t^{\frac{1}{n}} \tag{6}$$

where q_t is the amount of metal ion adsorbed at equilibrium (mg.g-1), K_F Freundlich equilibrium constant and C equilibrium metal concentration.

TABLE I:
PARAMETER VALUES OF ISOTHERM MODEL

Metal	Isotherm model	Parameters	25°C	35°C	45°C	55°C
Cobalt	Freundlich	n	3.86	2.74	2.54	2.2
		R ²	0.94	0.93	0.94	0.9
		K _F	37.70	17.67	11.22	10.48
	Langmuir	q _m	121.95	99.00	73.54	61.34
		R ²	0.99	0.98	0.98	0.99
		K _L	0.13	0.12	0.11	0.11
Cobalt	Freundlich	n	1.85	1.81	1.75	1.70
		R ²	0.95	0.93	0.95	0.94
		K _F	1.99	1.90	1.20	1.18
	Langmuir	q _m	47.84	46.39	30.30	24.87
		R ²	0.97	0.96	0.97	0.97
		K _L	0.02	0.02	0.02	0.01

Table I shows the experimental data obtained from the separation of cobalt from nickel ions onto modified clinoptilolites fitted well in Langmuir model with high correlation coefficient (R²) and maximum adsorption capacity for cobalt 121.95 and nickel 47.39. modified clinoptilolites [14].

K. Kinetic Studies

The kinetic study plays an important role because it gives important insight of the reaction mechanism:

- Pseudo first order model (see Eq. 7)

$$\frac{d q}{d t} = K_a (q_x - q_t) \tag{6}$$

- Pseudo second order model (see Eq. 7)

$$\frac{d q}{d t} = K_b (q_x - q_t)^2 \tag{7}$$

where K_a is the rate constant of pseudo first order model and k_b is rate constant of the pseudo second order model (hr⁻¹), q_x is the amount of metal ion adsorbed at time t (mg.g⁻¹) and q_t is the amount of metal adsorbed at equilibrium (mg.g⁻¹).

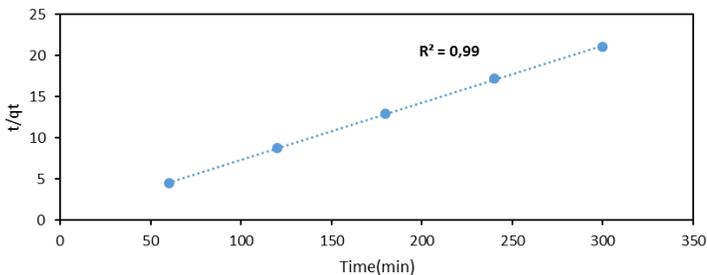


Fig. 11. Kinetics for cobalt removal onto modified clinoptilolites

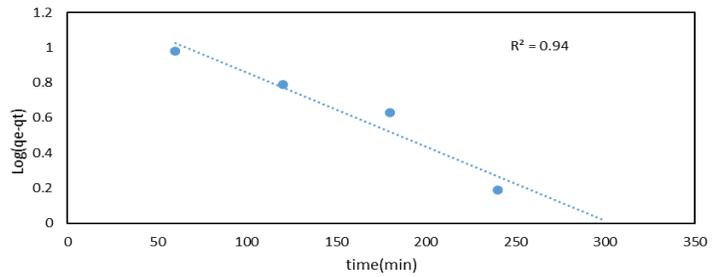


Fig. 12. Kinetics for cobalt removal onto modified clinoptilolites

Table II gives the values parameters of pseudo first and pseudo second order kinetic model. It was observed that the pseudo second order described well the kinetic model data with (R²) correlation coefficient was 0.99 (Borandegi & Nezamzadeh-Ejhi, 2015).

TABLE II: PARAMETER VALUES OF KINETIC MODEL

Metal	Pseudo first order		Pseudo second order	
Cobalt	q _e (mg/g)	53.30	q _e (mg/g)	100.1
	K ₁ (min ⁻¹)	2.89	K ₂ (g/mg.min)	0.014
	R ²	0.89	R ²	0.99
Nickel	q _e (mg/g)	8.81	q _e (mg/g)	18.37
	K ₁ (min ⁻¹)	2.91	K ₂ (g/mg.min)	0.020
	R ²	0.91	R ²	0.99

L. Thermodynamic studies

$$\Delta G^o = -RT \ln K_d \tag{8}$$

K_d is equilibrium constant that can be used to determine the thermodynamic parameters (H^o) enthalpy, (S^o) entropy and (G^o) the change in free energy.

where K_d is the distribution coefficient (mLg⁻¹), R (8.314 Jmol⁻¹/K) universal gas constant and T is the temperature (°K).

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \tag{9}$$

$$\Delta G = \Delta H - T\Delta S \tag{10}$$

$$K_d = \frac{q_e}{C_e} = \frac{(C_a - C_b)}{C_a} x \frac{V}{M} \tag{11}$$

where C_a and C_b are the initial ion concentration and final ion concentration of the solution, respectively and V and M are the volume of solution (mL) and amount of sorbent (g), respectively

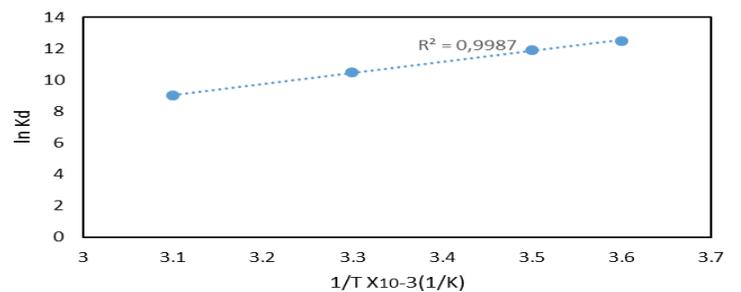


Fig. 13. Linearized

TABLE III: THERMODYNAMIC PARAMETERS FOR COBALT REMOVAL ONTO MODIFIED CLINOPTILOLITE

Temperature (K)	ln K _d	ΔG (kJ/mol K)	ΔH (kJ/mol K)	ΔS (kJ/mol K)
298	12.39	-59.71		
308	11.42	-59.04	-72.45	-50.47
318	10.87	-58.74		
328	9.67	-58.79		

The results in Table III show that ΔG° become less negative with the increase of the temperature that indicate the process is less favorable at high temperatures. The negative ΔG° values at different temperatures indicated that the reaction was thermodynamically feasible and spontaneous process. The negative ΔH° value confirmed that the reaction is exothermic and the negative value of ΔS° indicate that after cobalt adsorption on the modified clinoptilolites total entropy of the system decreased degree of disorderliness at the solid/liquid interface during the adsorption [14].

IV. CONCLUSION

This study indicates that the separation of cobalt and nickel using modified clinoptilolites with EDTA and succinic acid depends on cobalt initial concentration and some other parameters such as pH, mass of the adsorbent and temperature. Modified clinoptilolites can separate cobalt and nickel using ion exchange process. Particle size of the modified clinoptilolites showed also a significant role on the removal efficiency.

The characterization of clinoptilolites before and after modification was done using Scanning Electron Microscope (SEM), Fourier Transform Infrared spectroscopy (FTIR), X-ray fluorescence (XRF) and X-ray diffraction (XRD). The results showed that the separation of cobalt from nickel strongly depend on pH, initial concentration, mass of the adsorbent, particle sizes and temperature. High separation efficiency was obtained under following conditions pH 6, initial concentration 600 mg/L, mass of the adsorbent 10 g, particle sizes 1mm and temperature 25°C. The equilibrium sorption isotherms were analyzed by the Langmuir and Freundlich. The results showed that Langmuir isotherm describes better the adsorption process. The pseudo-first and second order model were used in analyzing kinetic data, absorption kinetics obeyed the second Pseudo order model that indicate that the rate limiting step for the process involves chemical reaction. Thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°) and entropy change (ΔS°) were calculated and negative results revealed that the process was spontaneous and exothermic.

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REFERENCES

[1] D.W. Nyembe, B.B. Mamba and A.F. Mulaba-Bafubiandi. "Adsorption mechanism of Co^{2+} and Cu^{2+} from aqueous solutions using natural

clinoptilolite: equilibrium and kinetics studies". *J. Appl. Sci.*, vol. 10, pp. 599-610, 2010.

- [2] M.E. Asio "Use of clinoptilolites for the removal of nickel ions from water: kinetics and thermodynamics". *J. Hazard. Mat.*, vol. 150, pp. 587-595, 2009.
- [3] T. Z. Sadyrbaeva Riga. "Separation of cobalt (II) from nickel (II) by a hybrid liquid membrane- electro dialysis process using anion exchange carriers", *Desalination*, vol.365, pp. 167-175, 2015.
- [4] F. Douglas, "Cobalt- nickel separation in hydrometallurgy, chemistry for sustainable development", vol. 12, pp. 81-91, 2004.
- [5] V. Coman. B. Robotin and P. Ilea, P (2013)" Nickel recovery/removal from industrial wastes, *Resources*", *Conservation and Recycling*, vol. 73, pp. 229- 238, 2013.
- [6] Al Dwairi and Rawajfeh, "Removal of cobalt and nickel from wastewater by using jordan low-cost zeolite and bentonite", *Chemical Technology and Metallurgy*, vol. 6, pp. 69-76, 2012.
- [7] M. Culfaz and M. Yagiz, M. "Ion exchange properties of natural clinoptilolite". *Separation and Purification Techn.*, vol. 37, pp. 93-105, 2004.
- [8] J. Kabuba and A.F. Mulaba-Bafubiandi, "Modelling of Co-Cu elution from clinoptilolites using neural network". *World Academy of Science Engineering and Technology*, vol. 68, pp. 1222-1225, 2012.
- [9] T. Ünalđı, I. Mızrak and S. Kadir, "Physicochemical characterisation of natural K-clinoptilolites and heavy-metal forms from Gördes", *Molec. Structure*, vol., pp. 349-358, 2013.
- [10] J. Ran, L. Wu, Y. He, Z. Yang, Y. Wang, Ch. Jiang, L. Ge, E. Bakangura, T. Xun. "Ion exchange membranes: New developments and applications", *Membrane Sci.*, vol. 13, pp. 267-291, 2017.
- [11] N. Öztürk, F. Uçun, A.D. Muhtar and S. Bahçeli, (2009) Infrared and SEM analyses of polyethyleneglycol-400 adsorbed on zeolites NaA, CaA, NaX and NaY, *molecular of structures*, vol. 14, pp. 35-38, 2009.
- [12] Borandegi and Nezamzadeh-Ejehieh, 2015.
- [13] M.V. Dinu and E. S. Dragan, "Evaluation of Cu^{2+} , Co^{2+} and Ni^{2+} ions removal from aqueous solution using a novel chitosan/clinoptilolites composite: Kinetics and isotherms Maria, *chemical engineering*, vol. 16, pp. 157-163, 2010.
- [14] L. Zhang, Y. Zeng Y and Z. Cheng. "Removal of heavy metal ions using chitosan and modified chitosan", *Molecular Liquids*, vol. 17, pp.175-191, 2016.