Selectivity of Clinoptilolite Towards Heavy Metals from Industrial Wastewater: Equilibrium, Kinetic, Thermodynamic and Elution Studies

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***Abstract*—Natural clinoptilolite was modified with dialkylphosphinic and succinic acid for the selective removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}. The natural and modified materials were characterized using x-ray diffraction (XRD), x-ray fluorescence (XRF), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FTIR) analysis. Batch experiment was conducted as a function of contact time, pH, clinoptilolite mass and temperature. The higher removal efficiency was obtained under the following optimal conditions: contact time 240 min, pH 6, the mass of modified clinoptilolite 6 g and temperature 45°C. The experimental data fit satisfactory to Langmuir and Dubinin-Radushkevich (D-R) isotherm models as well as pseudo-second order kinetic. Thermodynamic parameters such as Gibb's free energy change ($\Delta G°$), enthalpy change ($\Delta H°$), and entropy change ($\Delta S°$) were calculated. The ion exchange process was found to be spontaneous, endothermic and randomness. The selectivity of clinoptilolite towards heavy metals from industrial wastewater was in the sequence: $Co^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Fe^{2+}$. The effect of the acid concentration in elution was also investigated.**

***Index Terms*— Clinoptilolite, selectivity, heavy metals, Industrial wastewater, elution**

I. INTRODUCTION

THE presence of heavy metals such as cobalt, chromium, lead, copper, zinc, nickel and iron in industrial wastewater is a grievous environmental problem. These heavy metals are not biodegradable, being effortlessly accumulated in living organisms [1]. They can be the source of illnesses includes cancer, increases in blood and respiratory pressure, harmful to the nervous system, kidney failure and could become lethal at elevated concentrations [2-4]. Consequently, the pollution of water due to the presence of heavy metals is a crucial concern. Therefore, the removal of these metals is a subject of great social relevance because of the economic and environmental benefits of eliminating contaminates from industrial wastewaters. Simultaneous removal of a mixture of several heavy metals offers a cost-effective solution. It has been, however, quite challenge to date due to the completing removal of these heavy metals. Meanwhile, it is highly requested so as to avoid the repeated one by one removal of metals and of course to develop an attractive low-cost strategy. To accomplish this, several methods such as precipitation [5], electro-chemical precipitation [6], ion-exchange [7-11], membrane electrolysis [12], oxidation [13], solvent extraction [14, 15], adsorption [16, 17], coagulation flocculation and flotation [18] were suggested for the removal of heavy metals from aqueous solutions. All these methods have considerable disadvantages, which are partial removal, production of toxic sludge or waste products that required disposal and high energy consumption [5, 19] as well as being a very complicated operation with high cost of filtration for the selectivity of heavy metals [20, 21]. Ion-exchange is highly effective, low-cost, efficient and easy to operate amidst the physicochemical treatment processes. Furthermore, ion-exchange is effective for the removal of heavy metal ions from industrial effluent including those with a low concentration of heavy metals [22-24]. Therefore, selective removal of metal ions can be distinguished. In this way, numerous ion-exchange materials have been developed and employed. Although they may be effective for heavy metals removal. Natural zeolites are environmentally and economically acceptable hydrated aluminosilicate materials with exceptional ion-exchange and sorption properties. The excess of the negative charge on the surface of zeolite, which results from isomorphic replacement of silicon by aluminium in the primary structure unit [25]. Diverse studies so far have confirmed their excellent performance on the removal of heavy metals from wastewaters [25]. Natural zeolites are divided into different types (Analcime, Laumontite, Philipsite, Erionite, Chabazite, Natrolite, Mordenite, Heulandite, Clinoptilolite) according to their crystal structure, based on morphology, their physical properties, different ways of binding secondary units in the three-dimensional framework, the free pore volume and types of exchangeable cations in zeolite structure [25]. Clinoptilolite has been selected among the zeolites due to its a huge implementation in diverge fields more exclusively for the removal of heavy metals with his particular properties such as substantial specific area, low cost-effective, eco-friendly, high exchange capacity and microporous structure [26-33]. Clinoptilolites selectivity correlated to heavy metals is an important property in wastewater treatment procedure. Selectivity is a property of the exchanger to show different preferences for particular ions and it depends on field strength and with higher Si content [25]. However, the efficiency of clinoptilolite modified with dialkylphosphinic

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Manuscript received July 03, 2020; revised November 25, 2020. This work was supported in part by the Department of Chemical Engineering, Vaal University of Technology, South Africa.

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and succinic acid as ion-exchange material for the selective removal of Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} from industrial wastewater, has not investigated before and this emphasize the novelty of the current work. Moreover, it must mention that the removal of metal ions depends on numerous factors such as pH, mass dosage, contact time and temperature. In this present work, the modified clinoptilolite was characterized using XRF, FTIR, XRD, BET and SEM analysis. Furthermore, kinetic mechanism, equilibrium isotherm models and thermodynamic parameters were investigated.

II. EXPERIMENTS

A. *Materials and Solution*

The natural clinoptilolite employed in this study was supplied by Pratley Mining Company in South Africa. The solution was collected from the mining effluent in Mpumalanga province, South Africa. The pH of the solution was adjusted with hydrochloric acid and sodium hydroxide. Modification of clinoptilolite was done using dialkylphosphinic and succinic acid. All the chemicals used were analytical grade reagents from Sigma Aldrich.

B. *Treatment and modification of clinoptilolite*

Clinoptilolite was first cleaned with distilled water to remove fines and impurities then dried in the oven at 75℃ for 24 hours. Clinoptilolite was crushed in an agate mortar and screened through analytical sieves, for separating particle ≤ 100 µm for the characterization process and particle size of +1.0 mm for the removal process. Clinoptilolite was heated at 70℃ on a magnetic stirrer for 6 hours to eliminate magnetic impurities. To reach a fixed water content, after centrifuging and drying, the powder was stored in a desiccator for two weeks. An amount of 200 g of clinoptilolite were modified with 400 mL of 2M dialkylphosphinic acid at 60℃ for 24 hours, followed by washing it in deionized water. Clinoptilolite was then added to 400 mL of 2M succinic acid for 24 hours. Finally, the treated samples were centrifuged and washed with deionized water after which it was dried at room temperature.

C. *Instruments and characterization methods*

The heavy metals content in the solution were determined using Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES, Thermo scientific ICAP 7000). The elemental composition of the clinoptilolite was determined using X-Ray fluorescence (XRF, Philips Magix pro). The functional groups present in the clinoptilolite was determined using Fourier transform infrared spectroscopy (FTIR, Varian 7000). The morphological structure of the clinoptilolite was studied using scanning electron microscopy (SEM, Philips XL 30FEG). The surface area and pore volume were measured using Brunauer Emmett Teller gas adsorption analyzer (BET, Trister V6.06).

D. *Removal of Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} in batch experiment*

The removal of heavy metals from industrial waste solutions with modified clinoptilolite was performed in a Shaking Incubator at 185 rpm for 5 hours. A mass of modified clinoptilolite (2-10 g) was placed in a conical flask with 250 mL solution containing Co^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+} and Fe^{2+} at the following conditions: concentrations, temperature of 25- 55ºC, pH between 3 and 9 and contact time 60- 300 mins. A solution of 25 mL of the suspension was taken and filtered from the mixture; the resultant solutions were analyzed using Inductively coupled plasma atomic emission spectroscopy (ICP-AES).

Heavy metal ions percentage removal (R) and the metal ion (q_t) were calculated using Eqs. (1) and (2), respectively.

$$R = \frac{(C_i - C_t)}{C_i} x100 \quad (1)$$

$$q_t = \frac{(C_i - C_e)}{M} V \quad (2)$$

where C_i and C_t are the initial and equilibrium concentrations of metal ions (mg/L), respectively. V and M are the volume of the solution (L) and amount of clinoptilolite (g), respectively. All removal experiments were reproduced three times, and the mean values used. If the standard errors were greater than 0.01, the test was repeated to control the errors.

E. *Isotherm Models*

To determine the nature of the interaction between all tested metal ions and clinoptilolite, and find the maximum capacity of these, the adsorption data were examined using adsorption isotherms such as Langmuir, Freundlich and Dubinin- Radushkevich.

The Langmuir isotherm model is well described in a linear form as presented in Eq. (3) [34].

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m B_L} \quad (3)$$

where q_e is the amount of ion adsorbed at equilibrium by per unit weight of adsorbent (mg/g); C_e is the equilibrium concentration (mg/L), q_m is the amount of ion required to occupy the available site in the unit weight of the solid sample. The Langmuir monolayer adsorption capacity (mg/g), B_L is the Langmuir constant (L/mg). The parameters of Langmuir model were calculated from the slop-intercept of the plot of C_e/q_e versus q_e.

The Freundlich isotherm model is described in the linear form as seen in Eq. (4) [17].

$$log q_e = log K_F + \frac{1}{n} log C_e \quad (4)$$

where K_F and 1/n are Freundlich constants relating to the adsorption capacity and adsorption intensity, respectively. The value of n should be in the range of 1 to 10. The Parameters from this model was calculated from the slope -intercept of the plot log q_e versus log C_e.

The Dubinin-Radushkevich isotherm model offers a three parameter- equation, used to represent solute adsorption data on heterogeneous surfaces [1].

$$ln q_e = ln q_{max} - k\beta^2 \quad (5)$$

where q_e is the amount of ion adsorbed in (mg/g), q_{max} is the D-R monolayer capacity(mg/g), k is energy constant in (mol^2/kJ^2) and β is the Polanyi potential which is related to the equilibrium concentration which is defined in Eq. (6).

$$\beta = RTln\left(1 - \frac{1}{C_e}\right) \quad (6)$$

where R is the gas constant 8.314 in kJ/mol.K, T is the temperature in K. The slope of the plot of ln q_e versus β gives k (mol^2/kJ^2) and of the intercept yields the adsorption capacity q_{max} (mg/g). The energy required to remove each molecule of metal ions from the solution to the adsorption site can be calculated using Eq. (7).

$$E = \frac{1}{\sqrt{-2K_{ad}}} \quad (7)$$

The value of free energy E is vital and can be obtained in the nature of the adsorption process. If the value of E is ≤ 8 kJ/mol, the adsorption process is physical, but if it is between 8 and 16 kJ/mol, then it can be explained by ion exchange mechanism [35].

F. Kinetic of the process

Adsorption kinetics expresses how fast the chemical reaction occurs and gives details on the factors influencing the rate of reaction. Various researchers applied the first-pseudo-order kinetics of Lagergren and second-pseudo-order kinetics [36] as well as the intra-particle-diffusion model [37] as shown in Eqs. (8) to (10). These models are applied to investigate the controlling mechanism of the adsorption process.

$$log(q_e - q_t) = logq_e - \frac{k_1}{2.303}t \quad (8)$$

where q_e and q_t represent the amount of heavy metal ions adsorbed in (mg/g) at equilibrium and at time t, respectively. k_1 is the rate constant of the pseudo-first-order kinetics. The value of the adsorption rate constant, k_1 can be calculated from the straight-line plot of log (q_e-q_t) versus t.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e}t \quad (9)$$

where k_2 is the rate constant of pseudo-second-order models and it was calculated from the plot t/q_t and time. The pseudo-second-order model assumes that the rate-limiting step may be chemical adsorption involving valences forces through sharing or exchange of electrons between the clinoptilolite and aqueous solution [38]. The degree of goodness of the linear plot of these kinetic models can be judged from the value of the coefficient of determination of the plot, which can also be regarded as the criterion in the determination of adequacy of a kinetic model [39, 40]. The Intraparticle diffusion model is very vital in that it is the rate limiting step in any adsorption system [41]. In a proper batch system, the intraparticle diffusion has been applied in analyzing the adsorption process taking place in porous adsorbent [42]. Assuming the plots of (q_t) which is the amount of metal adsorbed per unit mass (mg/g) versus ($t^{0.5}$) square root of time are linear and pass through the origin. The deviation from the origin means the intra-particle is not the rate limiting step [43]. The intra-particle diffusion model is expressed in Eq. (10).

$$q_t = k_I t^{0.5} + C \quad (10)$$

where k_I is the intra-particle diffusion rate constant (g/mg/$min^{0.5}$) and C is the intercept.

G. Error analysis

To demonstrate the adequacy of the pseudo-first order and pseudo-second-order models, Marquardt's percent standard deviation (MPSD) test of statistical analysis was applied. The Marquardt's percent standard deviation was expressed in Eq. (11).

$$MPSD = 100\sqrt{\frac{1}{N-P}\sum_{i=1}^{n}\left(\frac{(q_{e(exp)} - q_{e(pred)})^2}{q_{e(exp)}}\right)i} \quad (11)$$

where N is the number of measurements, P stands for the number of parameters in the model, and $q_{e(pred)}$ and $q_{e(exp)}$ are predicted and experimental uptake rates, respectively.

H. Thermodynamic studies

In the present study, thermodynamic parameters such as Gibb's free energy change (ΔG°), enthalpy change (ΔH°), and entropy change (ΔS°) were calculated using Eqs. (12), (13) and (14).

$$lnK_d = \frac{\Delta S^o}{R} - \frac{\Delta H^o}{RT} \quad (12)$$

$$\Delta G^o = \Delta H^o - T\Delta S^o \quad (13)$$

where K_d is the distribution coefficient (mLg^{-1}).

$$K_d = \frac{q_e}{C_e} \quad (14)$$

The plot of ln K_d versus 1/T gives a straight line and the value of enthalpy change ΔH^o and entropy change ΔS^o can be calculated from intercept and slope, respectively.

III. RESULTS AND DISCUSSIONS

A. Characterization techniques

A.1. XRF analysis

The XRF analysis results of the natural and modified clinoptilolites with dialkylphosphinic and succinic acid are presented in Table I. The elemental composition results showed that the percentage composition of SiO_2 in the natural clinoptilolite was 73.6% and increased to 82.6% after modification. XRF characterization also reveals that both natural and modified clinoptilolites contain SiO_2, Al_2O_3, Na_2O, CaO, K_2O, Fe_2O_3 and MgO with percentage reduction in percentage composition of Al_2O_3, Na_2O, CaO, K_2O, Fe_2O_3 and MgO after modification with acid. The reduction in percentage compositions is attributed to the reaction between these compounds and dialkylphosphinic and the succinic acid used for modification. The reaction of CaO and the acid leads to the formation of soluble $CaCl_2$ [44]. The chemical composition reveals that the leaching of Fe^{3+} from the natural clinoptilolite depends strongly on the leaching of Ca^{2+}. It can be seen apparent that when more calcium is excluded from the clinoptilolite, Fe^{3+} is hindered. It is known that Fe^{3+} is affected by ions contained in the liquid phase, this is attributed to the formation of elements that can affect the kinetics of ion-exchange and selectivity of the clinoptilolite [45]. The composition of TiO_2 remains unchanged after the modification, which indicates that there is a small interaction between the acid and this compound [46]. Based on the elemental analyses of the natural and modified clinoptilolite samples, the modification process with acids affected the crystallinity of clinoptilolite. The ratio of Si/Al was 4.63 and increased to 6.35 after modification. The Si/Al ratio of the Heulandite type phase is low in the natural clinoptilolite, the high Si/Al ratio for the modified clinoptilolite can be attributed to the existence of hypothetical silica cristobalite. The exchangeable cation in the heulandite type is Ca^{2+}, K^+ and Na^+. The ratio $Ca^{2+}/(K+Na)$ is equal to 0.87 and 0.53 for the natural and modified clinoptilolites, respectively. This is due to the presence of feldspars as confirmed by XRD patterns.

TABLE I
CHEMICAL COMPOSITION OF NATURAL AND MODIFIED CLINOPTILOLITES

Metal oxide in (%)	Natural clinoptilolite	Modified clinoptilolite
SiO_2	73.61	82.6
Al_2O_3	13.52	11.2
K_2O	4.24	2.94
Fe_2O_3	1.60	0.35
CaO	3.65	2.11
Na_2O	0.83	0.15
MgO	0.70	0.19
TiO_2	0.21	0.21
Ratio Si/Al	**4.63**	**6.35**
Ratio Ca/(K+Na)	**0.87**	**0.53**

A.2. XRD analysis

Fig. 1 describes the XRD profiles of the natural and modified clinoptilolite samples. The typical characteristic peaks in 2θ values of 10.00°,13.47°, 17.62°, 22.46°, 25.95°, 26.94°, 30.17° and 32.02° observed in Fig. 1 are in agreement with the clinoptilolite crystalline structure presented in the literature by Kabuba and Rutto [8]. The pattern of natural clinoptilolite in Fig. 1A, suggested that the main mineral is heulandite with the peaks at 10.00 and 25.95° more intense than the remaining peaks of the pattern which are attributed to the presence of anorthite and mordenite [44]. As elucidated in Fig. 1B, the XRD patterns of modified clinoptilolite with dialkylphosphinic and succinic acid showed a decrease in peak intensity with the presence of amorphous materials which shifted to 9.96°, 10.04°, 26.27°, 27.00°, 28.26°, 30.11°, 32.07°, 32.86° and 36.94° in 2θ values. The patterns showed that the modified clinoptilolite implies the presence of heulandite, anorthite, and the co-existence significant amount of hypothetical silica, cristobalite and feldspars.

A.3. FTIR analysis

As shown in Fig. 2A, the peak at 690 cm^{-1} is because of the bending vibration of (Si-O-Al) and (Si-O-Si), whereas the peak at 795 cm^{-1} is because of the (Si-O) stretching vibration. Asymmetric vibration of (Si-O-Si) appeared at 1000 cm^{-1}. The peak at 1680 cm^{-1} is attributed to the presence of zeolitic water and the peak at 2840 cm^{-1} is ascribed to free hydrogenation water and intermolecular hydrogen bonding (zeolitic water) and the broad peak at 3500 cm^{-1} is ascribed to the bending and stretching vibration of hydroxyl groups (O-H). FTIR spectrum in Fig. 2B shows the peak at 665 cm^{-1} is due skeleton deformation vibration of the alkyl molecule for modified clinoptilolites. The peaks at 710 and 890 cm^{-1} are ascribed to (N-O) stretching vibration and (C-N-O) bending vibration, respectively. Peaks at 1220 and 1345 cm^{-1} are ascribed to asymmetrical vibration of CH_3. Peaks in the range of 1500 to 1800 cm^{-1} are ascribed to (N-O) and (C=O) stretching vibration [48]. The peak at 3465 cm^{-1} is attributed to the bending and stretching vibration of (O-H). There is an increase in intensity between 750 cm^{-1} and 1750 cm^{-1} indicating that modification has taken place. The peak at 1000 cm^{-1} is due to (Si-O-Al) and (Si-O-Si) stretching vibration which is also the major peak observed in the natural clinoptilolite because it is possible for an ion exchanger to maintain the same properties after modification [35]. This confirms the modification of clinoptilolite.

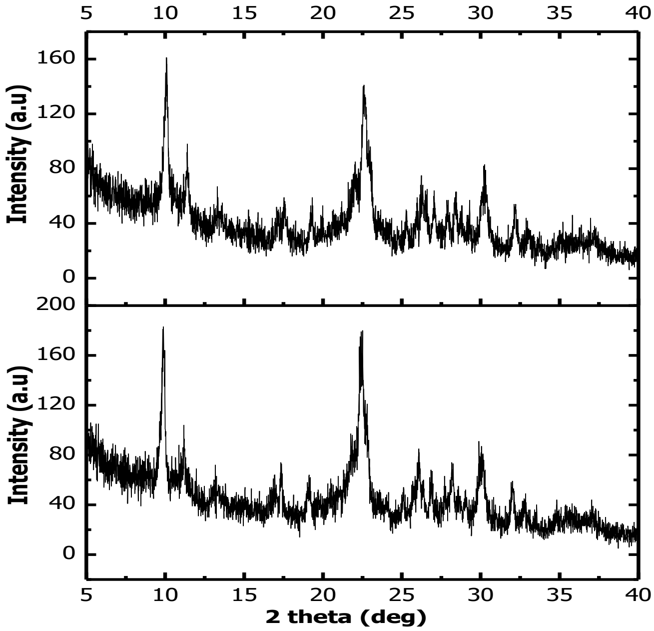

Fig. 1. X-ray diffraction pattern of (A) natural clinoptilolite and (B) modified clinoptilolite with dialkylphosphinic and succinic acid.

A.4. SEM analysis

SEM analysis was employed to scrutinize the change in the morphological structure of the clinoptilolite. The SEM image of natural and modified clinoptilolites with dialkylphosphinic and succinic acid were displayed in Figs. 3A and 3B, respectively. The SEM image of natural clinoptilolite indicates the presence of bigger globular particles with irregular shapes. After modification, as observed in Fig. 3B, cavities of different shapes and sizes had larger pores between the particles. The image exhibits a well-developed and littles glassy spherical particle, with an external surface which is full of cavities. This indicates that the modification on clinoptilolite was successfully reached. The main purpose of this modification was to increase the ion exchange capacity on the surface of the clinoptilolite and allowed the selectivity of heavy metal ion removal [8, 46].

A.5. BET analysis

The BET surface area, pore volume and pore size values of natural and modified clinoptilolites with dialkylphosphinic and succinic acid are presented in Table II. Natural clinoptilolite had a surface area of 35.32 m^2/g and pore volume of 0.068 cm^3/g and pore size of 17.32 nm while modified clinoptilolite had 40.07 m^2/g and pore volume of 0.076 cm^3/g and pore size of 13.76 nm. Clearly, the modified clinoptilolite sample had larger BET surface area and pore volume than the natural clinoptilolite, indicating that the COO− were intercaled into the natural clinoptilolite. However, with a significant increase in the BET surface area and pore volume, the pore size decreased after the modification. This could be attributed to the formation of new micropores during the modification process.

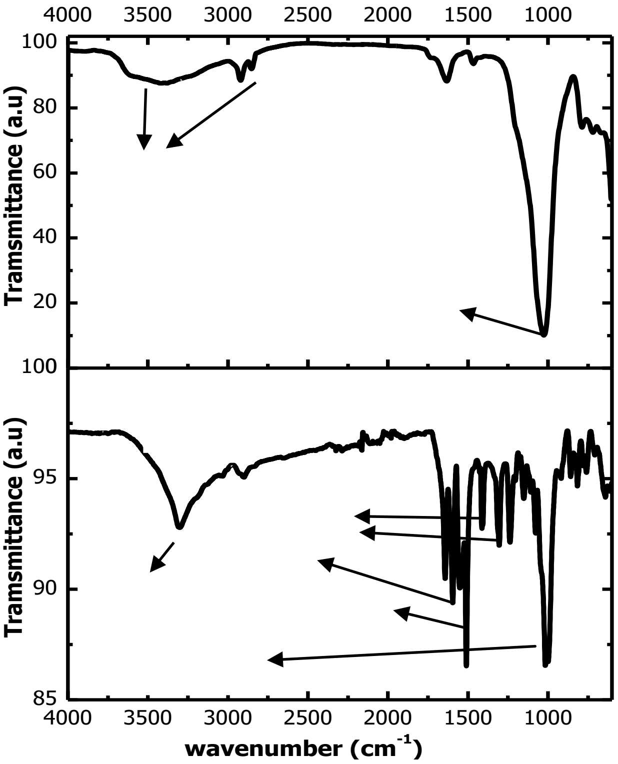

Fig. 2. FTIR spectra of (A) natural clinoptilolite and (B) modified clinoptilolite with dialkylphosphinic and succinic acid

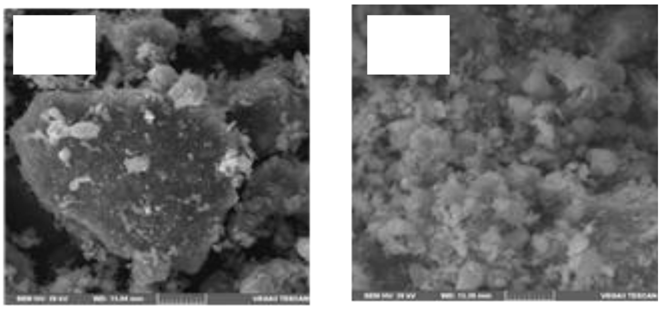

Fig. 3. SEM image of natural clinoptilolite (A) and modified clinoptilolite with dialkylphosphinic and succinic acid (B)

TABLE II

BET SURFACE AREA, PORE VOLUME, PORE SIZE OF NATURAL AND MODIFIED CLINOPTILOLITE

Clinoptilolite	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
Natural	35.32	0.068	17.35
Modified	40.07	0.076	13.76

B. Removal studies of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} in batch experiment

To research the efficiency of the modified clinoptilolite in heavy metals removal, parameters such as pH, contact time, dosage have been studied.

B.1. Effect of contact time

The effect of contact time in the removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} by modified clinoptilolite with dialkylphosphinic and succinic acid was studied over a range of 60−360 min and the results are given in Fig. 4. The percentage removal for metal ions increases with increasing contact time and remain constant after equilibrium. Equilibrium was reached at 240 min for Co^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}, while 300 min is required for Fe^{2+} to approach equilibrium. At the equilibrium time, the surface of clinoptilolites becomes saturated with respective metal and the removal efficiency becomes almost constant. The order of removal of metals on modified clinoptilolite under the same condition is Co^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Fe^{2+}. Percentage removal at the optimum condition was found as 93% Co^{2+}, 69% Cu^{2+}, 57% Zn^{2+}, 35% Ni^{2+} and 28% Fe^{2+}. The difference in percentage removal of different heavy metal ions at the same conditions (pH, clinoptilolite mass and contact time) is attributed to the difference in their chemical affinity and ion exchange capacity concerning the chemical functional group on the surface of the clinoptilolite [19].

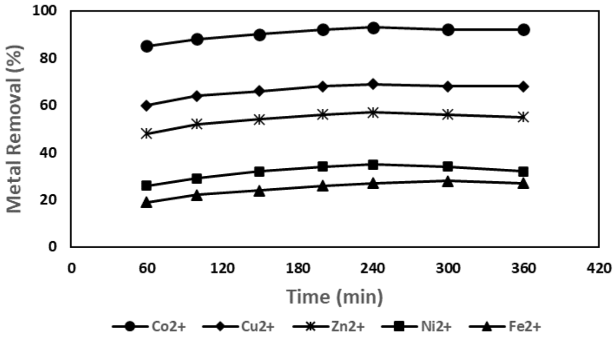

Fig. 4. Effect of contact time at the following parameters: pH 6, mass clinoptilolite 6g and temperature 45°C.

B.2. Effect of pH solution

The pH is one of the most significant factors controlling the ion-exchange process of metal ion onto modified clinoptilolite. The influence of pH on the removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} onto modified clinoptilolite with dialkylphosphinic and succinic acid was studied over a pH range of 2−8. Fig. 5 shows the percentage removal increase from 82.50% to 96% for Co^{2+}, 70% to 81 % for Cu^{2+}, 62.50% to 77% for Zn, 52% to 62% for Ni^{2+} and 42% to

50% for Fe^{2+} with increasing of the pH from 2 to 6. At lower pH values, the number of hydrogen ions is high and Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} ions have to compete with them for available sites on the clinoptilolite surface. High percentage removal at pH 6 indicated a high affinity for metal ion Co^{2+} predominant in this region. Increasing pH further may cause precipitation of metal ions as hydroxide.

B.3. Effect of Dosage

Dosage is an important parameter in the ion exchange process because it influences the capacity of modified clinoptilolite at a given initial concentration. The effect of clinoptilolite mass on the removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} was studied using the mass of modified clinoptilolite of 1−10 g. Fig. 6 shows that on increasing the mass of modified clinoptilolite from 1 to 6 g the percentage removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} increased from 81% to 95%, 60 % to 65%, 43% to 49%, 24% to 31% and 14.50% to 20%, respectively. This trend is attributed to the increase in active site on the modified clinoptilolite making adsorption more favorable to Co^{2+} as compared to other metal ions [37]. There was no significant change observed as the clinoptilolite mass was further increased. This was due to the concentration of metal ions that reached equilibrium.

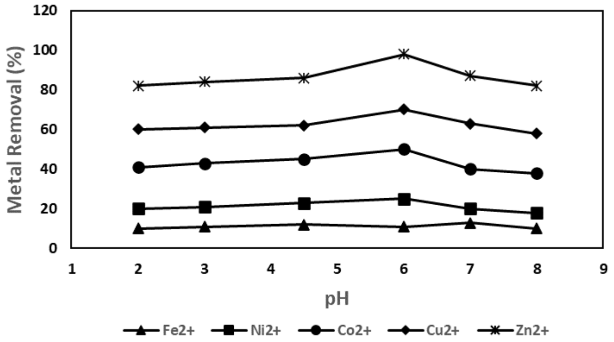

Fig. 5. Effect of pH at the following parameters: time 240 min, mass clinoptilolite 6g and temperature 45°C.

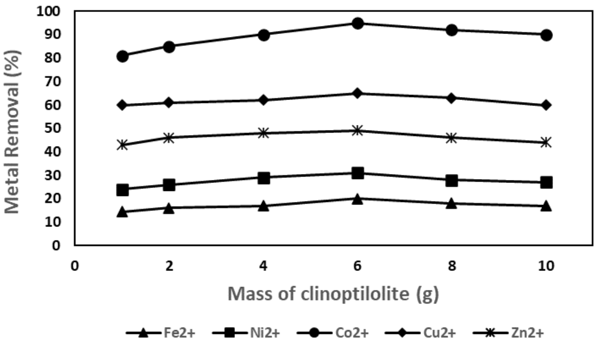

Fig. 6. Effect of mass of clinoptilolite at the following parameters: pH 6, time 240 min, mass clinoptilolite 6g and temperature 45°C.

B.4. Effect of temperature

Temperature is an important variable in this process, and it can affect the solution/solid interface as well as the kinetic characteristics of the process. The removal of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} by modified clinoptilolite with dialkylphosphinic and succinic acid was studied in the range 25- 55°C as shown in Fig. 7. The increase in percentage removal was from 83% to 92.50%, 64% to 74%, 60% to 70%, 24% to 36.50% and 20.50% to 30% for Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}, respectively, with temperatures ranging from 25 to 55 ℃. This may be attributed to either the increase in the number of active sites available or desolvation of the adsorbing species and the decrease in the thickness of the boundary layer surrounding the modified clinoptilolite. Since the diffusion is an endothermic process, greater removal percentage was observed at a higher temperature. Thus, the diffusion rate of ions in the external mass transport process increases with temperature [48].

C. Selectivity studies

Modified clinoptilolite with dialkylphosphinic and succinic acid was used for the recovery of some transition metal cations including Cu^{2+}, Co^{2+}, Ni^{2+}, Fe^{2+} and Zn^{2+} from industrial waste solution. The efficiency of modified clinoptilolite for the removal of the investigated ions in Figs 4-7 reach a maximum at contact time 240 min, pH 6, clinoptilolite mass of 6 g and temperature of 45℃, obeying the following trend:

$Co^{2+} > Cu^{2+} > Zn^{2+} > Ni^{2+} > Fe^{2+}$.

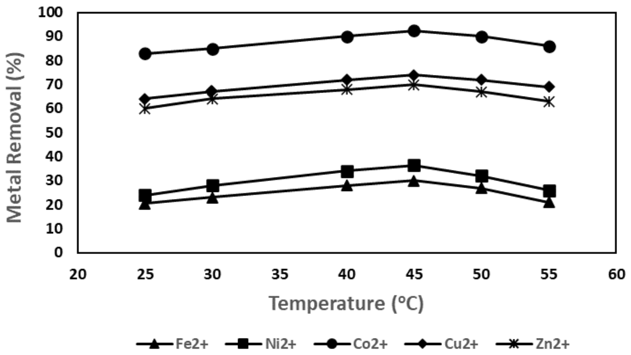

Fig. 7. Effect of temperature at the following parameters: pH 6, time 240 min, mass clinoptilolite 6g and temperature 45°C.

The removal of heavy metal ions using natural clinoptilolite obeys the following trend: $Zn^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Fe^{2+}$ which can be explained by the ionic radius of cations [49]. It would be expected that cations with a smaller hydrated radius can easily lose a part of its hydrated radius to enter the pore modified clinoptilolite pores. Also, complete fitting of the cations in the clinoptilolite cavity causes greater cation exchange capacity. Based on the results presented in Figs. 4-7, the best removal efficiency was obtained for Zn^{2+} by the natural clinoptilolite. There is a difference between the recovery efficiency of the natural and modified clinoptilolites, especially for Co^{2+} removal. These observations confirm that in the modified clinoptilolite there is a complexation process which is responsible for the selective recovery, in addition to ion exchange, as the only process occurred for the natural clinoptilolite. This also could be explained from the hard-intermediate-soft-acid-base principle (Pearson Law), hard metal cations such as Pb^{2+}, Mg^{2+} and Al^{3+} will interfere in Co^{2+} recovery due to a stronger interaction with hard COO−(carboxylic groups) of modified clinoptilolite. While other soft and intermediate cation such as Cu^{2+}, Ni^{2+} and Cr^{2+} have little affinity for modified clinoptilolite on the Co^{2+} removal.

D. *Isotherm studies*

From these results, the adsorption of the tested ions is well described by the Langmuir isotherm model. D-B model values for all studied metal ions were higher than 8 kJ/mol., confirming that the attractive forces were chemical bonding (chemisorption). The isotherm parameters for Langmuir, Freundlich and D-R models are presented in Table III. The Langmuir model (Fig. 8A) was successful in analyzing data of all the heavy metals ions studied with R^2 values ≥ 0.98. The adsorption capacity in (mg/g) onto modified clinoptilolite followed an increasing sequence of Fe^{2+} (11.36) < Ni^{2+} (13.25) < Zn^{2+} (16.59) < Cu^{2+} (20.85) < Co^{2+} (29.39), whereas B_L in (L/mg) determines the affinity of modified clinoptilolite sites for Co^{2+} and the trend followed an increasing order of Fe^{2+} (0.013) < Ni^{2+} (0.016) < Zn^{2+} (0.146) < Cu^{2+} (0.208) < Co^{2+} (0.407). This trend can be explained regarding electron affinity and electronegativity since the adsorption of these cations is due to ion exchange at the surface. The electronegativity of Co, Cu, Zn, Ni and Fe (Pauling scale) are 1.91, 1.90, 1.65, 1.91 and 1.83, respectively, which agrees with the order of affinity.

The Freundlich model presented in Fig. 8B did not fit well in analyzing experimental data of Co, Cu, Zn, Ni and Fe with $R^2 < 0.90$. The K_F in values (mg/g) decreased in the order of Co^{2+} (11.32) > Cu^{2+} (9.43) > Zn^{2+} (7.36) > Ni^{2+} (5.98) > Fe^{2+} (4.35); the n values indicate favorable adsorption for the considered cations.

The D-R model showed in Fig. 8C was successful in analyzing experimental data for the considered metal ions with R^2 values ≥ 0.94. The adsorption capacity in (mg/g) onto modified clinoptilolite followed a decreased sequence of Co^{2+} (15.59) > Cu^{2+} (12.42) > Zn^{2+} (11.69) > Ni^{2+} (10.21) > Fe^{2+} (9.82). The energy values for these ions are respectively, 15.59, 11.42, 10.69, 10.21 and 8.82 kJ/mol. These values indicate that the process is described by ion exchange mechanism.

TABLE III
LANGMUIR, FREUNDLICH AND DUBININ RADUSHKEVICH ISOTHERM PARAMETERS FOR MODIFIED CLINOPTILOLITE WITH DIALKYLPHOSPHINIC AND SUCCINIC ACID AT 318K

Model	**Parameters**	**Co^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Ni^{2+}**	**Fe^{2+}**
Langmuir	q_m (mg/g)	29.39	20.85	16.59	13.25	11.36
	K_L (L/mg)	0.408	0.208	0.146	0.016	0.013
	R^2	0.990	0.990	0.980	0.990	0.980
Freundlich	n	4.700	2.220	2.310	1.980	2.590
	K_F (mg/g)	11.32	9.430	7.360	5.980	4.350
	R^2	0.840	0.850	0.850	0.840	0.820
D-R	q_s (mg/g)	22.52	14.35	11.15	9.75	8.960
	E (kJ/mol)	15.59	11.42	10.69	10.21	8.820
	R^2	0.950	0.960	0.940	0.940	0.910

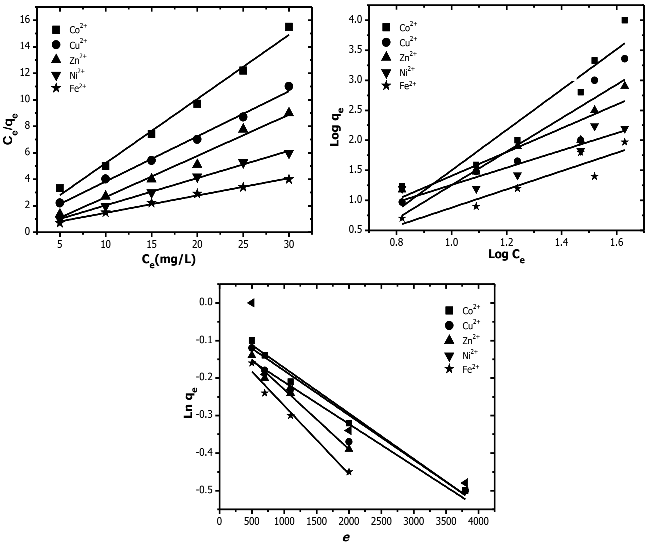

Fig. 8. Langmuir (A), Freundlich (B) and Dubinin- Radushkevich isotherm (C) parameters for modified clinoptilolite with dialkylphosphinic and succinic acid.

E. *Kinetic studies*

The sorption kinetics was investigated for better understanding of the dynamics of sorption of metals on the modified clinoptilolite. The plot of pseudo-first order, pseudo-second order and intraparticle diffusion models for recovery of assessed metal ions (Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}) onto modified clinoptilolite with dialkylphosphinic and succinic acid is presented in Figs. 9A-C.The values of the parameters in each case as well as the MPSD (M) values are presented in Table IV. The R^2 values for pseudo-second order and intraparticle model are higher and closer to 1 in comparison to pseudo-first order. This observation indicates that the pseudo-second order and intraparticle model described best the kinetic data of cations assessed. The low MPSD (M) values for pseudo-second-order kinetic model signifies coherence to predicted and experimental data and high MPSD (M) values from pseudo first order signifies poor coherence to predicted and experimental data. This statistical model of analyzing data demonstrates the suitability of the pseudo-second order model. The rate constant of pseudo-second order followed a decreasing sequence of 0.073, 0.042, 0.038, 0.033 and 0.021 Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}, respectively.

TABLE IV
KINETICS PARAMETERS FOR CONSIDERED METALS IONS ONTO MODIFIED CLINOPTILOLITE

	Ions	**Co^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Ni^{2+}**	**Fe^{2+}**
Pseudo first order	K_1	0.110	0.070	0.050	0.030	0.020
	R^2	0.860	0.840	0.910	0.890	0.820
	M	34.23	31.52	16.56	12.32	6.790
	q_e	28.88	20.51	16.52	13.85	11.05
Pseudo second order	K_2	0.073	0.042	0.038	0.033	0.021
	R^2	0.990	0.980	0.990	0.980	0.990
	M	3.980	4.320	3.980	3.780	6.180
Intra particle diffusion	K_I	0.131	0.103	0.075	0.041	0.035
	R^2	0.960	0.950	0.970	0.970	0.980

F. Thermodynamic studies

The contents experimental data obtained at different temperatures (298-328K) was used to calculate the thermodynamic parameters such as ΔH^o, ΔG^o, ΔS^o, using Eqs. (12), (13) and (14).

The plot of ln K_d vs 1/T for the recovery of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} onto modified clinoptilolite is presented in Fig. 10. The calculated values of thermodynamic parameters are presented in Table V. The ΔG^o values were negative for entire temperature range studied, this suggests that the process is spontaneous. A similar finding was reported by Borandegi and Nezamzadeh-Ejhieh [37]. These values are lower than 18 kJ/mol, characteristic of a physisorption [1, 50]. The positive enthalpy confirms the endothermic behavior and the entropy positive values indicate an increase in the randomness in the clinoptilolite/liquid interface during the adsorption of metal ions onto modified clinoptilolite.

TABLE V

THERMODYNAMIC PARAMETERS FOR THE ADSORPTION OF METAL IONS

	T°	**Co^{2+}**	**Cu^{2+}**	**Zn^{2+}**	**Ni^{2+}**	**Fe^{2+}**
ΔH^o		19.43	35.65	21.56	9.400	9.98
ΔS^o		50.47	28.56	18.28	14.63	6.12
ΔG^o	298	-17.47	-6.81	-5.34	-5.54	-4.29
	303	-18.56	-6.85	-5.37	-5.58	-4.17
	313	-22.77	-6.56	-5.44	-5.72	-4.13
	318	-22.91	-6.42	-5.87	-5.49	-4.03
	328	-21.13	-6.10	-5.72	-5.43	-3.97
R^2		0.980	0.970	0.960	0.970	0.950

G. Heavy metals elution

The effect of the acid concentrations in elution was investigated. The elution of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} from the loaded modified clinoptilolite was carried out using sulphuric and hydrochloric acids. For 60 min, 5.00 g of clinoptilolite loaded with 4.90 mg/g of metals were put in contact with 30 mL of H_2SO_4 and HCl concentrations varied from 1M to 4M.

The uptake or elution efficiency (%) was calculated according to Eq. (1). Cobalt and nickel are always present together in waste and industrial solutions. They have similar chemical and physical properties [51], consequently, the percentage elution is the same of both acid concentrations as illustrated in Table VI. It was also observed that HCl elution is best accomplished with an acid concentration of 4 M for Zn^{2+} (85.34%) compare to H_2SO_4 with 83.64%.

As shown HCl was a very powerful metal-desorbing agent compared to H_2SO_4. An acid concentration higher than 4 M was not tested as it was feared that the stability of the clinoptilolite might be affected [12]. Zn^{2+} is easily eluted when compared to other metal ions due to its low charge density and hydrated ion diameter. Low charge density exhibits a high need for hydration [52]. Therefore, the high affinity of Zn^{2+} for the aqueous phase leads to a faster elution. Therefore, their high affinity for the aqueous phase leads the following selectivity: $Fe^{2+} < Co^{2+} < Ni^{2+} < Cu^{2+} < Zn^{2+}$.

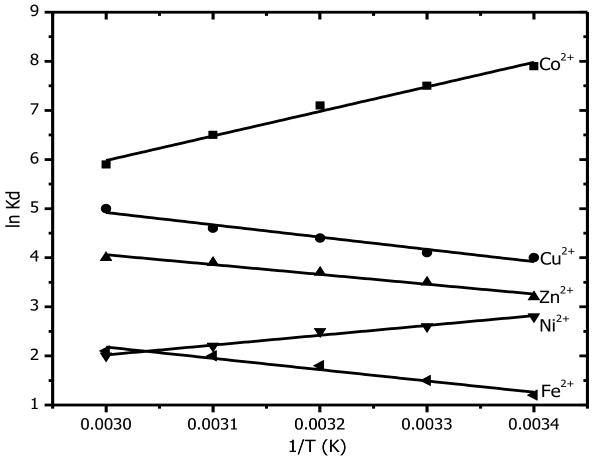

Fig. 10. Thermodynamic plot ln Kd vs 1/T for heavy metals onto modified clinoptilolite

TABLE VI

ELUTION PERCENTAGE

	H_2SO_4			**HCl**		
	1M	2M	4M	1M	2M	4M
Fe^{2+}	34.43	42.09	80.02	29.03	40.09	81.35
Co^{2+}	36.31	44.01	82.34	30.97	41.96	82.82
Ni^{2+}	36.31	44.01	82.34	30.97	41.96	83.83
Cu^{2+}	36.44	44.12	82.93	32.04	42.12	84.08
Zn^{2+}	38.99	46.98	83.64	33.87	44.98	85.34

IV. CONCLUSION

The results of this study indicated that modified clinoptilolite with dialkylphosphinic and succinic acids can be used for Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+} removal simultaneously from industrial waste solution. XRF, XRD, FTIR, BET and SEM analyses showed that chemical modification took place. The optimum condition was found to be contact time of 240 min, pH of 6, the mass of modified clinoptilolite of 6 g and temperature 45^oC. The equilibrium data at various temperatures fitted well the Langmuir and Dubinin- Radushkevich (D-R) isotherms. The kinetic study showed a great fit to the pseudo-second-order kinetic model in multi component systems, illustrating that the processes were chemisorptive in nature for all metal ions. It was also observed that the intraparticle diffusion played an important role in the recovery of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Fe^{2+}. The positive values of $\Delta H°$ for all metals ions indicate that the process is endothermic, negative values of $\Delta G°$ showed the spontaneous nature of the process and positive values of $\Delta S°$ reflect an increase in randomness at solid/solution interface during the sorption of metal ions onto modified clinoptilolite. The effect of the acid concentrations in elution was investigated, it was observed that HCl elution is best accomplished with an acid concentration of 4 M for Fe^{2+} (85.34%) compare to H_2SO_4 with 83.64%.

ACKNOWLEDGMENT

I would like to thank Ms Nomsa Baloyi for the characterization results.

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