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The Sequestration of Heavy Metals Contaminating the Wonderfonteinspruit Catchment Area using Natural Zeolite

P.P. Diale, S.S.L. Mkhize, E. Muzenda, and J. Zimba

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***Abstract*—**For more than 120 years, gold mining formed the backbone the South Africa's economy. The consequence of mine closure was observed in large-scale land degradation and widespread pollution of surface water and groundwater. This paper investigates the feasibility of using natural zeolite in removing heavy metals contaminating the Wonderfonteinspruit Catchment Area (WCA), a water stream with high levels of heavy metals and radionuclide pollution. Batch experiments were conducted to study the adsorption behavior of natural zeolite with respect to Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+}. The data was analysed using the Langmuir and Freudlich isotherms. Langmuir was found to correlate the adsorption of Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} better, with the adsorption capacity of 11.9 mg/g, 1.2 mg/g, 1.3 mg/g, and 14.7 mg/g, respectively. Two kinetic models namely, pseudo-first order and pseudo second order were also tested to fit the data. Pseudo-second order equation was found to be the best fit for the adsorption of heavy metals by natural zeolite. Zeolite functionalization with humic acid increased its uptake ability.

***Keywords*—**gold-mining, natural zeolites, water pollution, West Rand.

I. Introduction

GOLD (Au) mining extraction occurs from relatively narrow bands of quartzitic reefs, which were previously deposited as fluvial sediments in river deltas at the shores of an ancient inland lake [1]. In the case of uraniferous ores, the Au content in the ore is relatively lower compared to that of uranium (U) (i.e. about Au-U ratio 1:100), therefore large amounts of U and other heavy metals are brought to the surface by Au mining operations. Since mining is a transitory use of land that requires disruption or disturbance to provide essential mineral and energy [2]: land, hydrological, and air effects are always forthcoming. Acid mine drainage (AMD) is the most well documented type of water pollution associated with mining. Iron sulphides, also known as pyrite (FeS_2), are large contributors to AMD. The pyrite oxidation process can be summarized by these reaction sequences:

$$FeS_2 + 3.5O_2 + 2H_2O \rightarrow FeSO_4 + H_2SO_4 \quad (1)$$

$$4Fe^{2+} + 1/2\ O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \quad (2)$$

$$4Fe^{3+} + 12H_2O \rightarrow 4\ Fe\ (OH)_3\ (s) + 12H^+ \quad (3)$$

$$FeS_2\ (s) + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \quad (4)$$

P.P. Diale and E. Muzenda, and S.S.L. Mkhize are with the Department of Chemical Engineering, Faculty of Engineering and Built Environment, University of Johannesburg, Doornfontein, 2001, South Africa (e-mail: pdiale305@gmail.com and emuzenda@uj.ac.za).
J. Zimba is with Salene Tehnologies, Streathan House, Streatham Crescent, Bryansto, 2021, South Africa (jzimba@braeston.com)

In the first step, pyrite reacts with oxygen and water producing Fe^{2+} and sulphuric acid by reaction (1). The second step has the oxidation of Fe^{2+} to Fe^{3+} by reaction (2), which is pH-dependent. The third step corresponds to the hydrolysis of Fe^{3+} with water to form a ferric hydroxide precipitate and the release of additional acidity, which is promoted by the pH-dependent reaction (3). The fourth step is defined as the oxidation of additional pyrite by Fe^{3+} according to reaction (4). The pyrite oxidation process is controlled by bacterial species that have definite pH growth range and pH growth optimum [3]. The conversion of Fe^{2+} to Fe^{3+} has been described as the rate limiting step, however the presence of bacteria such as *Acidithiobacillus ferroxidans* is known to accelerate this reaction greatly. *Acidithiobacillus ferroxidans* is a common pyrite oxidizing bacterium and is the driving force behind the extensive acid and metal pollution generated when it releases metals from acid mine water [4].

A number of studies have been conducted using zeolites for removing heavy metals contaminating lake, streams, and dams [5], [6], and [7]. Zeolite was found to be effective in removing Pb^{2+} and Zn^{2+} from industrial wastewater at a pH of 7 [8]. Also zeolite has been found to be potentially effective for treating AMD [9], [10], [11], and [12]. Zeolites represent an appropriate material for removing heavy metal ions from water streams, because of its cation exchange characteristic.

The net negatively charged structure, which results from isomorphic substitution of Al^{3+} and Si^{4+} ions of the tetrahedral, with exchangeable cations such as Ca^{2+}, Na^+, or K^+ located in the cavities and channels within it, give zeolite its most valuable characteristic [13]. Zeolites are also characterized by large void volumes (20% - 50%) and large internal surface areas of several hundred square meters per gram [14], [15], [16], and [17]. The amount of metals removed by zeolite is affected by the free energy of hydration of the cations, the valence of the cations, the molecular size and hydrated radius of cations [18] and [19]. Taking into consideration these characteristics, we focus our attentions to the use of sorption isotherms and kinetic models to determine the efficacy of natural zeolite in treating heavy metal contaminated water bodies of the Wonderfonteinspruit Catchment Area (WCA).

II. Materials and Methods

The zeolite-rich samples from volcanic tuffs of Heidelberg area, Western Cape, South Africa, were examined by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), N_2-porosimetry in combination with Fourier transform infra-red (FTIR) spectroscopy. Prior to all analyses, the samples were pulverized and dried. A Leica-Cambridge Scanning Electron Microscope (Model S420-1) was used to study the surface morphology of the zeolite. X-ray powder diffraction patterns were obtained using a Siemens D500 diffractometer, with Ni-filter, Cu K_a radiation, operating at 40 kV, 30 mA. A step size of 0.02° 2θ and a counting time of 4 second per step were applied over a range of 3° to 90° 2θ. X-ray fluorescence analysis were carried out with the use of

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an ARL Advant XP sequential (wavelength dispersive) XRF. Nitrogen adsorption measurements were performed with a Micromeritics ASAP 2010 surface area analyzer. For the adsorption-desorption curves the adsorbate was N_2 and pore size distribution was calculated from the desorption branch using the Barret-Joyner-Halenda (BJH) model. The pre-treatment, which involves the degassing procedure of the samples, took place under the temperature of -195.850 °C. IR absorption measurements were carried out using a FTIR Perkin Elmer 880. The FTIR spectra in the wavelength ranged from 400cm^{-1}–5000 cm^{-1}.

Adsorption experiments for metals Fe^{2+}, Mn^{2+}, Ni^{2+}, and Zn^{2+} were carried out with 0.5 g initial mass of zeolite material, at initial pH values of 2.4 and at different initial metal concentrations: 5, 10, 25, 50, 100, and 130 mg/L. Tests were run for 120 minutes on an orbital shaker, enough time to reach equilibrium and all samples were analysed with an Atomic Absorption Spectrophotometer (AAS). The experimental design is summarised in Table 1.

TABLE I
EXPERIMENTAL PROGRAM FOR EXAMINING THE METAL ADSORPTIVITY BY NATURAL ZEOLITE

Inorganic salts	Concentration (mg/L)	pH	Agitation (rev/min)	Zeolite (g)	Vol. (mL)
Zinc Chloride ($ZnCl_2$)	6.9	2.4	180	0.5	50
Iron Sulphate ($Fe(SO_4)_2$)	115	2.4	180	0.5	50
Manganese Sulphate ($Mn(SO_4)_2$)	121	2.4	180	0.5	50
Nickel Sulphate ($Ni(SO_4)_2$)	26.5	2.4	180	0.5	50

The experimental results were fitted to the Langmuir and Freundlich sorption isotherm models. For the purpose of comparative study, the natural zeolite material was functionalized with humus, consisting of 20% humic acid and 2 % fulvic acid. Humic substances are chemically complex materials that have the capacity to remove metals from solutions. They contain carboxylic groups, phenolic and alcoholic hydroxyls, ketones and quinine groups, which all can react with metal and subsequently remove them from solutions. The process of zeolite functionalization is to introduce some if not all the groups found in the humic material, with an aim to improve its heavy metal removal capacity. Natural zeolite of 200 g mass was mixed with humic acid (20%) 250 ml in a 500 mL glass beaker. The mixture was stirred on a magnetic plate for 24 hours, filtered and washed before it was dried in an oven for 24 hours. The Fourier Transform Infrared (FTIR) was used to determine the extent of the functionalization of the zeolite material.

III. RESULTS AND DISCUSSION

3.1 Chacterisation of natural zeolite

The electron scanning was used to study the surface morphology of the zeolite material. Several large crystals together with amorphous materials formed a large pore mouth in Fig 1, depicting a heulandites group crystal complex. Thin platy crystals "coffin-shaped" ones indicate that the HEU type zeolite is not crystallized uniformly and that discrete crystals of heulandites and of clinoptilolite are mixed together contributing to what is macroscopically determined as "heulandites type-II" [20].

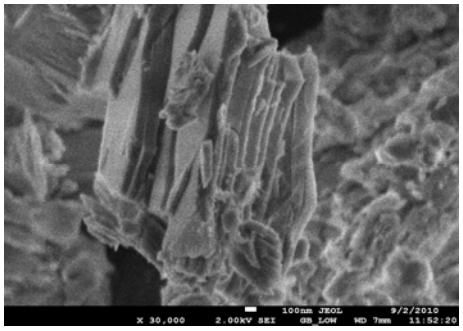


Fig. 1 SEM picture of Jadico zeolitic tuff

The main zeolite mineral belongs to the heulandites group. The (020) reflection of heulandites, at 9.98 Å is always far more intense than the remaining lines of the pattern, while the respective reflection of clinoptilolite, is found at about 3.98 Å. The indices of refraction and birefringence of heulandite type zeolites decrease with substitution of Na and Si for Ca and Al. Clinoptilolite has $n\alpha$ = 1.476 – 1.491, $n\beta$ = 1.479 – 1.493, $n\gamma$ = 1.479 – 1.497, δ = 0.003 – 0.006 and 2Vx = small to large [21].

The elemental analysis by X-ray fluorescene (XRF) was used to distinguish whether the natural zeolites were heaulandite or clinoptilolite type zeolites and whether they were hydrophobic or hydrophilic, a summary of these results are shown in Table 2.

TABLE II
ELEMENTAL ANALYSIS RESULTS OF JADICO ZEOLITE TUFF

SiO_2	Al_2O_3	K_2O	Fe_2O_3	CaO	TiO_2	Si /Al	Reference
17.8	2.7	2.0	1.3	0.7	0.1	6.59	This study
77.96	13.17	2.20	1.06	3.80	0.08	5.92	Ata et al., 1994
63.74	11.80	2.46	1.66	1.86		5.40	Ören et al., 2005 (Gordes zeolite)
73.6	13.5	4.24	1.60	3.65		5.45	Elaiopolous et al., 2007
58.75	24.31	3.64	7.55	0.43	1.09	2.42	Ríos et al., 2008

The results showed that the zeolite sample had a high silicon composition compared to aluminium. Potassium (K) and calcium (Ca) were the major single extra-framework cations in natural. According to IMA CONMMN's third rule, only heulandite and clinoptilolite zeolites can solely be distinguished on the basis of the silica and aluminium framework [22]. Heulandite has a Si/Al ratio of less than 4, whilst clinoptilolite has a Si/Al of equal or more than 4. The Si/Al ratio is 6.6 (mol/mol). The chemical composition, the theoretical exchange capacity, and the Si/Al ratio, generally ranging from 4 to 6.8, are typical for clinoptilolite. Low-silica members are enriched with calcium, whereas high-silica clinoptilolites are enriched with potassium, sodium, and magnesium. The advantage of

high Si/Al ratios is that in low pH environments, the structure is less likely to be damaged. The pore size distribution (PSD) was estimated using Barret-Joyner-Halenda (BJH) model and Table 3, shows the results.

TABLE III
POROSIMETRY STUDY RESULTS

Sample	BJH Desorption average pore diameter (nm)	BET surface area (m^2/g)
Jadico	10.36	65.48

The adsorption/desorption isotherm curves were used for determine the pore morphology of the difference zeolite material. Specific surface area was estimated using the Brunaer-Emme-Teller (BET) equation isotherm. According to literature, common industrial

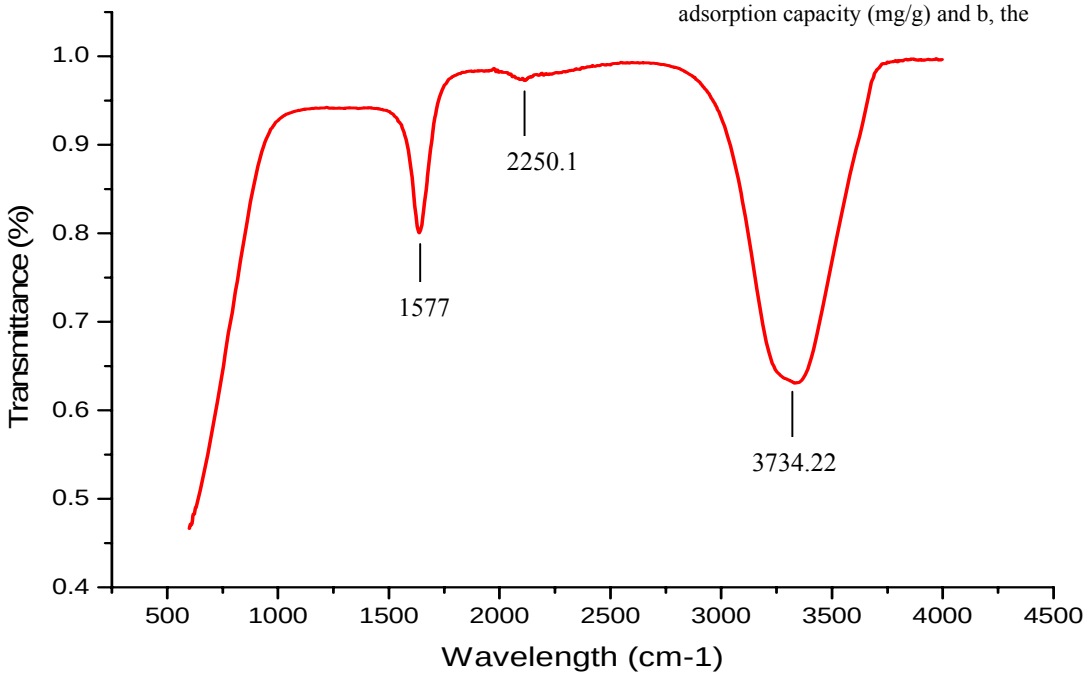


Fig. 2 FTIR spectrum of the Jadico zeolitic tuff

adsorbents like activated carbon have surface areas in the range of 500 m^2/g – 2000 m^2/g, with polymeric adsorbents having 150 m^2/g – 1000 m^2/g. For the natural zeolite analysed the surface areas was found to be 65.48 m^2/g. The surface area is lower than those of adsorbents currently used in the catalysis industry. This could imply that the use of natural zeolites in such applications may not be ideal. Fig. 2, shows the resulting spectra of the sample from the Jadico zeolitic tuff. The strongest T – O stretching vibration appears at 3734.22 cm^{-1}. The vibration in the region 1600 – 3700 cm^{-1} can be assigned to the presence of zeolite water molecules. This OH^- stretching is attributed to interaction between the water hydroxyl and cations present. Clinoptilolite gives a band at ~ 1059 cm^{-1}, while heulandites give a band at ~1022 cm^{-1} [23]. Thus, the clinoptilolite sample from Jadico tuffs presented at 1577 cm^{-1}. The other band, at 22550.1 cm^{-1} represents the presence of alkenes in the structure. The vibration in the region 1600 cm^{-1} – 3700 cm^{-1} can be assigned to the presence of zeolite water. The isolated OH^- stretching (3634.2 cm^{-1}) is attributed to interaction between the water hydroxyl and the cations present [23].

3.2 Adsorption study

The sorption data was subjected to different sorption isotherms, namely, Langmuir and Freundlich. The equilibrium data for metal cations over the concentration range from 10 mg/L – 130 mg/L at room temperature have been correlated with these isotherms. A linear plot is normally obtained when Ce/Qe is plotted against Ce over the entire concentration range of metal ions investigated, and this is illustrated in Fig. 3. The Langmuir model was derived on assumptions that: (i) maximum adsorption corresponds to a saturated monolayer of adsorbate molecule on the adsorbent surface; (ii) the adsorption sites and reactions have a constant free-energy change (ΔG^o_{ads}) for all and (iii) there is no transmigration of adsorbate in the plane of the surface [24]. With Langmuir two parameters will be analysed to evaluate the efficiency of the system: Qm, maximum adsorption capacity (mg/g) and b, the energy of adsorption (L/mg). This model has the form as follows:

$$Qe = Q\max\frac{bCe}{1+bCe} \quad (5)$$

$$\frac{Ce}{Qe} = \frac{1}{Q\max b} + \frac{Ce}{Q\max} \quad (6)$$

Where Qe (mg/g) is the amount adsorbed at equilibrium and Qmax (mg/g) is the Langmuir constant, which is equal to the adsorption

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capacity. The parameter *b* represents the Langmuir sorption equilibrium constant, and *Ce* (mg/L) is the equilibrium concentration.

The Langmuir model parameters and the statistical fits of sorption data to the isotherm equation are given in Table 4. The Langmuir model described the sorption data for all the cations with R^2 value > 0.9, except for Fe^{2+}.

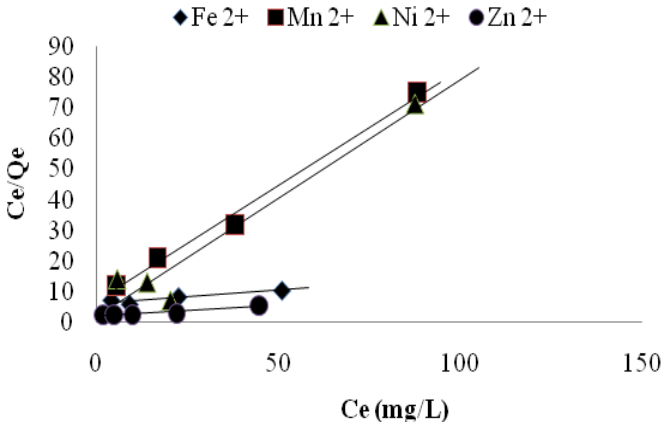


Fig. 3 Langmuir isotherm for metal removal by Clinoptilolite zeolitesites

According to the Q_{max} (mg/g) parameter, sorption on zeolite is produced following the sequence: Zn^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}. Zeolites are generally weakly acidic in nature and sodium-form exchangers are selective for hydrogen, which leads to high pH values when the exchanger is equilibrated with relatively dilute electrolyte solutions [25]. This then makes the metal hydroxide precipitation feasible. In natural zeolites these metals seem to reach saturation, which means that the metal had filled possible available sites and further adsorption could take place only at new surfaces [26].

Alternatively, the Freundlich equation is an empirical and is among the earliest empirical equations that can be employed to predict adsorption equilibria data. The Freundlich isotherm is based on these assumptions: (i) the adsorbent has a heterogeneous surface energy, where different sites could have different site energies, as opposed to the Langmuir assumption of constant site energy; (ii) the site energies for adsorption follow a Boltzmann distribution and the mean site energy = ΔH^{o}_{M} and; (iii) the change in adsorption site entropy increases linearly with increase site enthalpy ($-\Delta H^{o}_{ad}$) [27].

The Freundlich equation can be written in the following form:

$$\log Qe = \log K_f + \frac{1}{n}\log Ce \qquad (7)$$

Where, K_f and n are the Freundlich constants. The parameter K_f indicates the Freundlich adsorption capacity, while the parameter n characterizes the heterogeneity of the system. The parameter n is usually greater than unity. A larger n value, means that the system is more heterogeneous, which usually results in non-linearity of the adsorption isotherm. The Freundlich sorption isotherm was applied to the removal of Fe^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+}.The ability of the model to fit the experimental data was examined and a typical plot, as shown in Fig.4, was obtained for all metals investigated. The constants K_f and n were calculated for each cation (Table 4). This isotherm does not predict any saturation of the sorbent by the sorbate, thus infinite surface coverage is predicted mathematically, indicating multilayer adsorption on the surface [23]. The ion exchange capacity of heavy metal cations is listed in Table 4 indicates the following selectivity sequence: Ni^{2+} > Mn^{2+} > Zn^{2+} > Fe^{2+}. The heavy metal cations are present as hexaqua complex ions with six surrounding water molecules in the solution and pass through the zeolite framework in this form [28]. The adsorption

TABLE IV LANGMUIR AND FREUNDLICH ISOTHERMS PARAMETERS

	Langmuir Isotherm Model		Freundlich Isotherm Model	
Metal	R^2	Estimated Parameters	R^2	Estimated Parameters
Fe^{3+}	0.8456	Q_m = 11.933 (mg/g) b = 0.01371 (L/mg)	0.9773	K_f = 0.1874 (mg/g) n = 1.149
Mn^{2+}	0.9917	Q_m = 1.3126 (mg/g) b = 0.086 (L/mg)	0.9411	K_f = 0.126 (mg/g) n = 1.4535
Ni^{2+}	0.9362	Q_m = 1.286 (mg/g) b = 0.5693 (L/mg)	0.7723	K_f = 0.232 (mg/g) n = 2.192
Zn^{2+}	0.9157	Q_m = 14.728 (mg/g) b = 0.035 (L/mg)	0.9612	K_f = 0.5756 (mg/g) n = 1.286

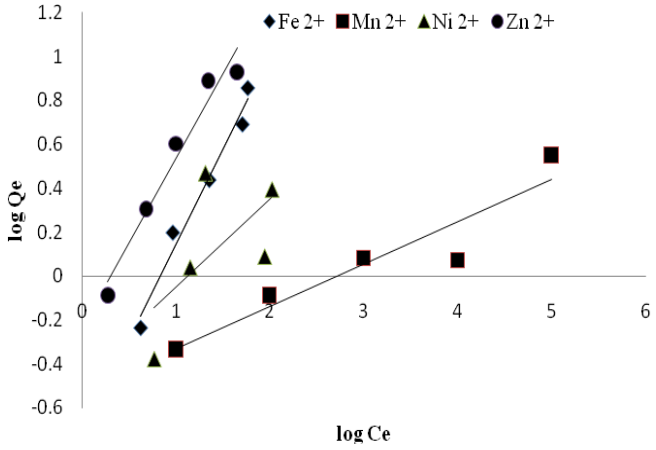


Fig. 4 Freundlich isotherm for metal removal by Clinoptilolite zeolite

phenomena depend on the charge density of cations; therefore the diameter of hydrate cations is very important [28]. The charges of the metal cations same (+2), Mn^{2+} ions (the biggest diameter) had the least adsorption and Zn^{2+} had the most adsorption.

3.3 Kinetic study

Two kinetic models were applied to evaluate the experimental data and results. The pseudo-first-order kinetic model for the adsorption of liquid/solid system is based on solid uptake capacity. This model assumes that the rate of uptake with time is directly proportional to the difference in the saturation concentration and the amount (cumulative) of solute uptake with time. The general equation is expressed as:

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$$\frac{dQ}{dt} = k(Qe - Q) \quad (8)$$

Where Qe and Q are the amounts of metal ions adsorbed on the adsorbent (mg/g) at equilibrium and at time t, respectively, and k is the pseudo-first order adsorption rate constant (min^{-1}). Integrating equation (8) for the boundary condition t = 0 to t = t and q = 0 to qt = qt, the linear form of the equation becomes,

$$\ln(Q_e - Q) = \ln Q_e - kt \quad (9)$$

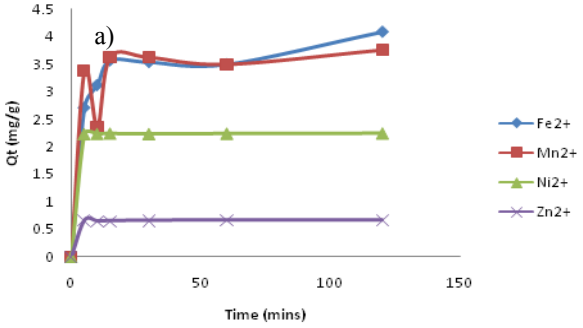
The plot of ln(Qe-Q) vs t would be a straight line its slope will give the value of specific rate constant. The pseudo-second-order kinetic model is based on the amount of adsorbate on the adsorbent. If the rate of adsorption is a second order mechanism, the pseudo-second-order chemisorption kinetics rate equation is expressed as:

$$\frac{dQ}{dt} = k(Q_e - Q)^2 \quad (10)$$

where *k* is the second-order adsorption rate constant (g mg^{-1} min^{-1}). Integrating equation (10) between the same limits, the linear form of the equation is written as:

$$\frac{t}{Q} = \frac{1}{kQ_e^{\ 2}} + \frac{1}{Q_e}t \quad (11)$$

The plot between t/Q vs t will be a straight line its slope and intercept will help to find the specific rate constant. The specific rate constant, determining the affinity for metal uptake, is directly proportional to the amount of metal ions adsorbed (*Qe*) by zeolite. The *Qe* value obtained from plots should be the same as the *Qe* abtained from kinetic models, in order for the model to be satisfied. The *Qe* calculated values, obtained from of pseudo-first-order kinetic model were extremely low and values are also fairly low when compared with the *Qe* experimental values for both natural and functionalized zeolite, see Table 5. The correlation coefficients for the pseudo-second-order kinetic model were more than 0.99 for all natural and functionalized zeolite and the theoretical metal capacity *(Qt)* values agreed well with the experimental metal capacity (*Qe)* values. This model is based on the assumption that the rate limiting stage can be a chemical adsorption involving valence forces through sharing or exchange of electrons between adsorbent and adsorbate. This appears to provide the best correlation of the obtained data. The kinetic data for the adsorption process illustrated in Figs 5(a) and (b), show that adsorption rate after humic acid functionalization is clearly higher for iron and manganese except for nickel and zinc.



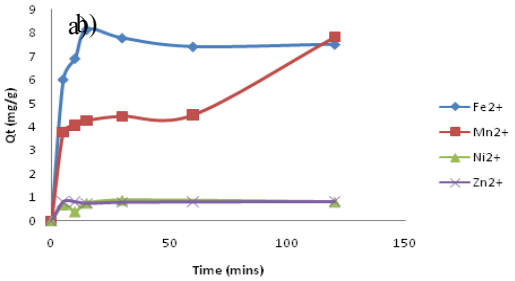


Fig. 5 (a) Metal uptake by un-functionalized zeolite , (b) Metal uptake by functionalized zeolite

TABLE V
KINETIC PARAMETERS FOR THE REMOVAL OF METALS WITH NATURAL AND FUNCTIONALIZED ZEOLITE

Zeolite	Pseudo-first-order model			Pseudo-second order model		
	K_1	Qe (mg/g)	R^2	Ki_2	Qe (mg/g)	R^2
Natural						
Fe^{2+}	0.004	2.19	0.124	0.08	4.1	0.993
Mn^{2+}	0.001	0.84	0.04	0.131	3.78	0.996
Ni^{2+}	0.0014	0.408	0.238	2.28	2.24	1
Zn^{2+}	0.0019	0.126	0.139	8.81	0.662	1
Functionalised						
Fe^{2+}	0.005	1.535	0.082	1.02	7.576	0.999
Mn^{2+}	0.001	0.884	0.1	0.29	4.57	0.999
Ni^{2+}	0.009	0.396	0.163	0.609	0.81	0.99
Zn^{2+}	0.02	0.491	0.25	2.39	0.822	0.999

Better results appear to be due to humic acid treatment that changes substantially the chemical composition of the treated zeolite for all heavy metals. The kinetic uptake (*Qe*) followed the sequence: $Fe^{2+} > Mn^{2+} > Ni^{2+} > Zn^{2+}$; for natural zeolite and $Fe^{2+} > Mn^{2+} > Zn^{2+} > Ni^{2+}$; for functionalized zeolite. The sequence of kinetic rate (*k*) showed a similar trend.

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IV. Conclusion

- The natural zeolitic tuff, Jadico, from the Western Cape, South Africa was found to belong to the clinoptilolite group zeolite.
- The sorption isotherms of Fe^{2+}, Mn^{2+}, Zn^{2+}, and Ni^{2+} fitted the Langmuir model. The metal uptake sequence was obtained as: $Zn^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$. Zinc had the highest maximum metal uptake at (14.728 mg/g). According to the equilibrium constant, the affinity of metals for the metal removal followed the sequence: $Zn^{2+} > Fe^{2+} > Mn^{2+} > Ni^{2+}$.
- The sorption of iron, manganese, nickel and zinc with natural and functionalized zeolite, fitted linearly to the pseudo-second order kinetic model, indicating that the process occurred in at least two steps. Zinc had the fastest sorption kinetic for both natural and functionalized zeolite. However, iron had the highest metal uptake.
- The natural zeolite functionalization by treating it with humic acid increased its uptake ability significantly for iron, manganese and not for zinc and nickel.

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Palesa Diale is a postgraduate student in the Chemical Engineering Department of the University of Johannesburg, doing her Master's degree (2010 -). Her research interest firmly lies with environmental management, which is a fantastic platform to actively apply chemistry along with coordinated scientific and engineering principles in order to provide antidotes to limit or prevent negative impacts of pollution, particularly that induced by mining activities.



Samukelisiwe Mkhize is a postgraduate student in the Chemical Engineering Department of the University of Johannesburg, whose completed here Btech degree with a cum laude in 2010. Her research interests firmly lies in 'green chemistry'and waste water treatment.



Edison Muzenda is the Research and Postgraduate Coordinator and head of Environmental and Process Systems Engineering Research Unit in the School of Mining, Metallurgy and Chemical Engineering at the University of Johannesburg, Dr Muzenda holds a BSc Hons (NUST, Bulawayo, ZIM, **1991 - 1994**) and a PhD in Chemical Engineering (University of Birmingham, Birmingham, United Kingdom, **1997 - 2000**).

He joined the University of Johannesburg, Johannesburg, South Africa on the 1st of November 2007. He has more than **15** years experience in academia which he gained at different Institutions: National University of Science and Technology Bulawayo, University of Birmingham, Bulawayo Polytechnic, University of Witwatersrand and University of Johannesburg. He is a recipient of several awards and scholarships for academic excellence. His research interests and area of expertise are in phase equilibrium measurement and computation, energy and environment, separation processes and mineral processing.

He has published more than **60** international peer reviewed papers in international scientific journals and conferences. His publications are mainly on measurement and computation of phase equilibrium using group contributions methods, static headspace and the dynamic GLC technique; flotation studies-effect of water quality, microwave pretreatment, pH; Leaching behaviour of copper bearing mattes; wastewater treatment, the characterization of South African zeolites for industrial and environmental applications and



Josephat Zimba is the General Manager for Salene Technologies, South Africa. Prior to that, he worked in the Advanced Materials Division at Mintek (South Africa) initially as a Senior Engineer and subsequently as a Principal Engineer. He holds a Doctorate in Physical Metallurgy and has nearly 15 years international experience in the field of Metallurgical/Materials Engineering. Josephat is a member of the Southern Africa Institute of Mining and Metallurgy and the USA Materials Research Society. In addition, he is a Fellow of the Zimbabwe Academy of Sciences and the current President of the Africa Materials Research Society.

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