Equilibrium ion exchange studies of Zn^{2+}, Cr^{3+} and Mn^{2+} on natural bentonite

International Conference on Industrial Waste & Wastewater Treatment & Valorization, 21-23 May 2015, Athens, Greece

IWWATV Industrial Waste & Wastewater Treatment & Valorisation

M.A. Stylianou, **V.J. Inglezakis**, M. Loizidou, A. Agapiou, G. Itskos

Astana, Kazakhstan

Nazarbayev University

NAZARBAYEV UNIVERSITY
SCHOOL OF ENGINEERING

http://seng.nu.edu.kz/seng/home

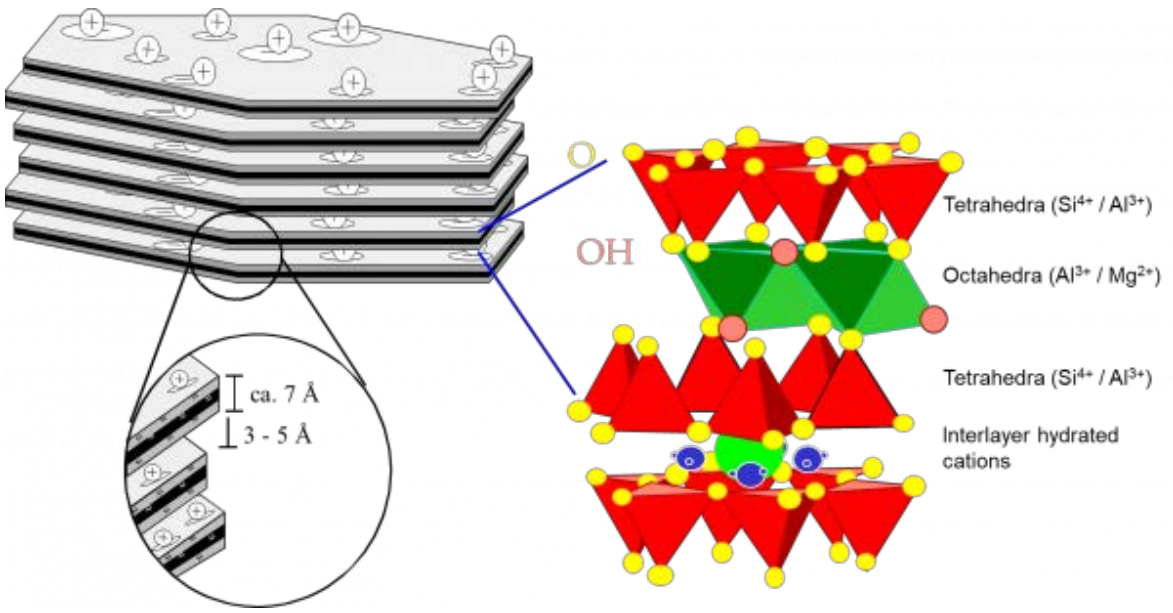
Aim of the study

- The aim of this study is to present equilibrium experimental data and apply simplified isotherm models for Zn^{2+}, Cr^{3+} and Mn^{2+} exchange on natural bentonite by using a rigorous experimental protocol.

Bentonite

- Bentonite is a clay mineral that is often used in ion exchange processes due to its high ion exchange capacity
- >50% montmorillonite

- Heavy metal adsorption on montmorillonite is achieved through:
  - (a) exchange of cations in the interlayers resulting from the interactions between ions and negative permanent charge and
  - (b) formation of inner-sphere complexes through $Si–O^-$ and $Al–O^-$ groups at the clay particle edges



Source: http://www.sandb.com/our-resources/bentonite/

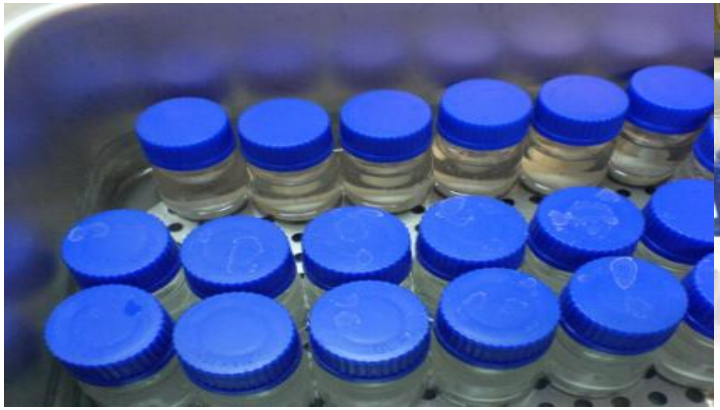
Materials and methods

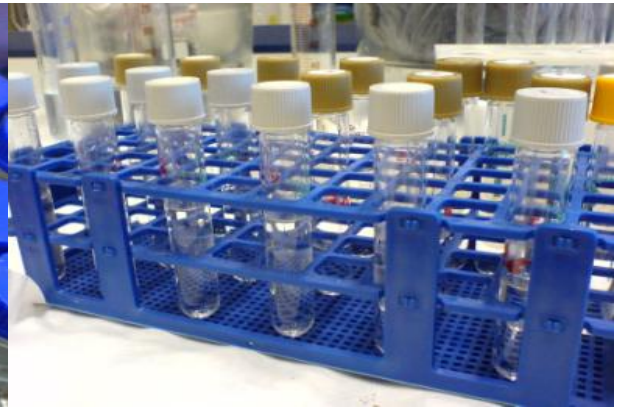
- The bentonite used was supplied by S&B Industrial Minerals SA (Greece) (<90μm).

- The chemical composition and characterization of the material was obtained through
  - XRD, XRF, FTIR, BET and TG/DTA methods
  - The mineral was used without any chemical pretreatment.
  - Samples before experimental investigation were air-dried at 80°C and then kept in desiccators

Materials and methods

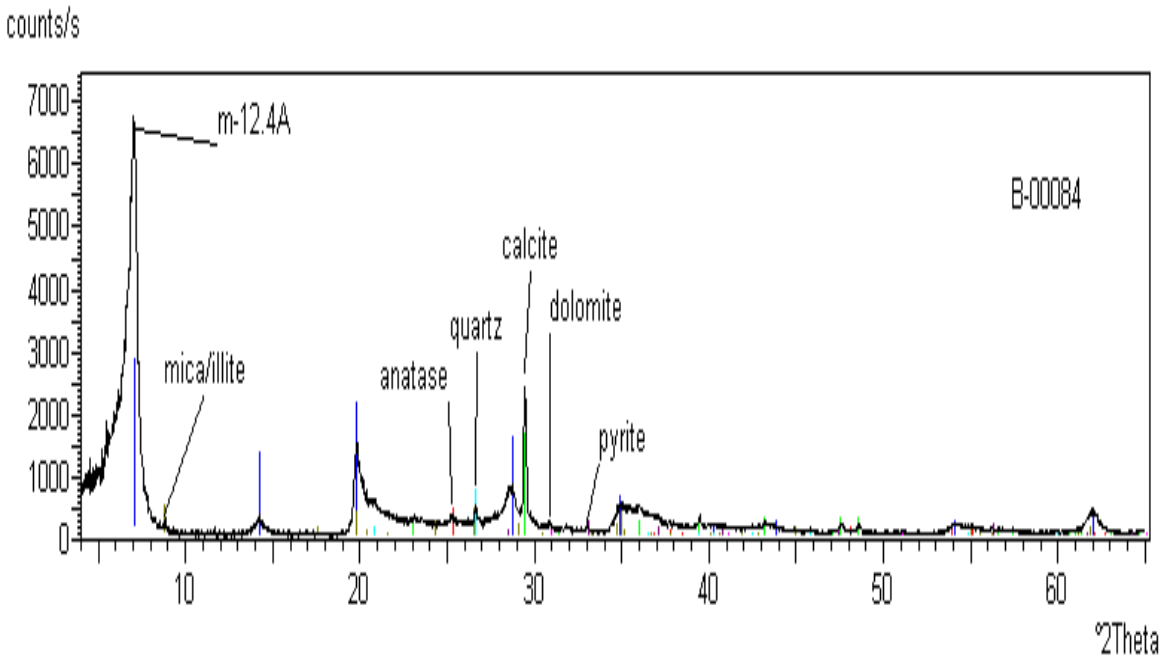
- Ion exchange equilibria of Zn^{2+}, Cr^{3+} and Mn^{2+} on bentonite was examined by
  - use of batch equilibrium isotherms,
  - distribution coefficients
  - maximum exchange levels and
  - sorption isotherms
- under the same normality for all metals (0.01 N) at 25±2°C, pH=4





Results

- XRD analysis of bentonite samples

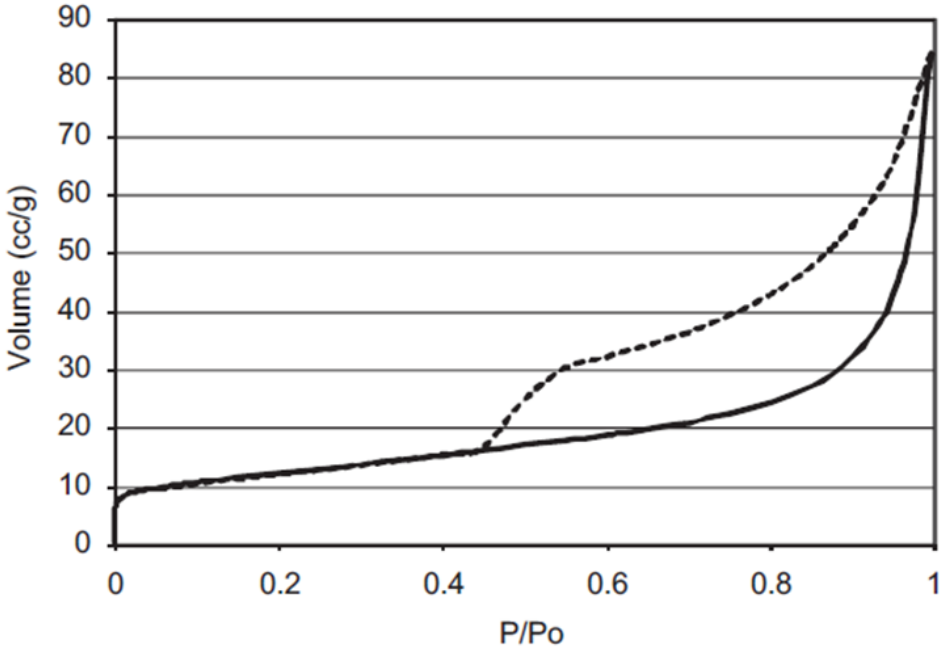


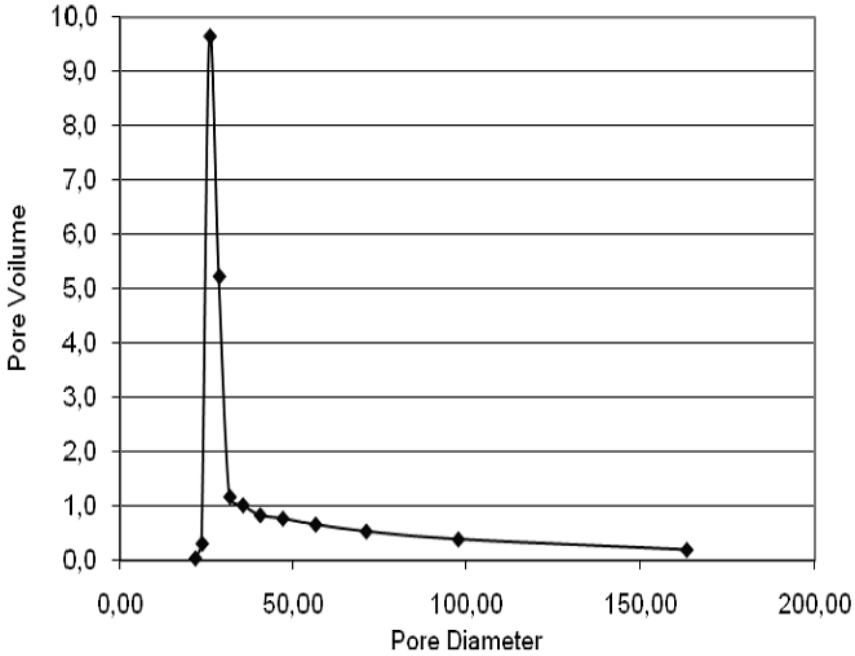
Bentonite chemical analysis (XRF)

Oxide	% w/w
SiO_2	55,9
Al_2O_3	18,0
Fe_2O_3	3,85
CaO	3,63
MgO	3,53
Na_2O	3,52
K_2O	0,611

Results - Sorption – Desorption isotherm curves (bentonite)

- BET surface area of bentonite is **41.87 m^2/g**, within the limits found in the literature for natural bentonites, between 20 to 69.34 m^2/g
- Type IV isotherms
  - characteristic of many mesoporous industrial adsorbents
- The presence of a broad hysteresis loop in the desorption isotherms reveals the existence of limited ordered meso-macroporosity

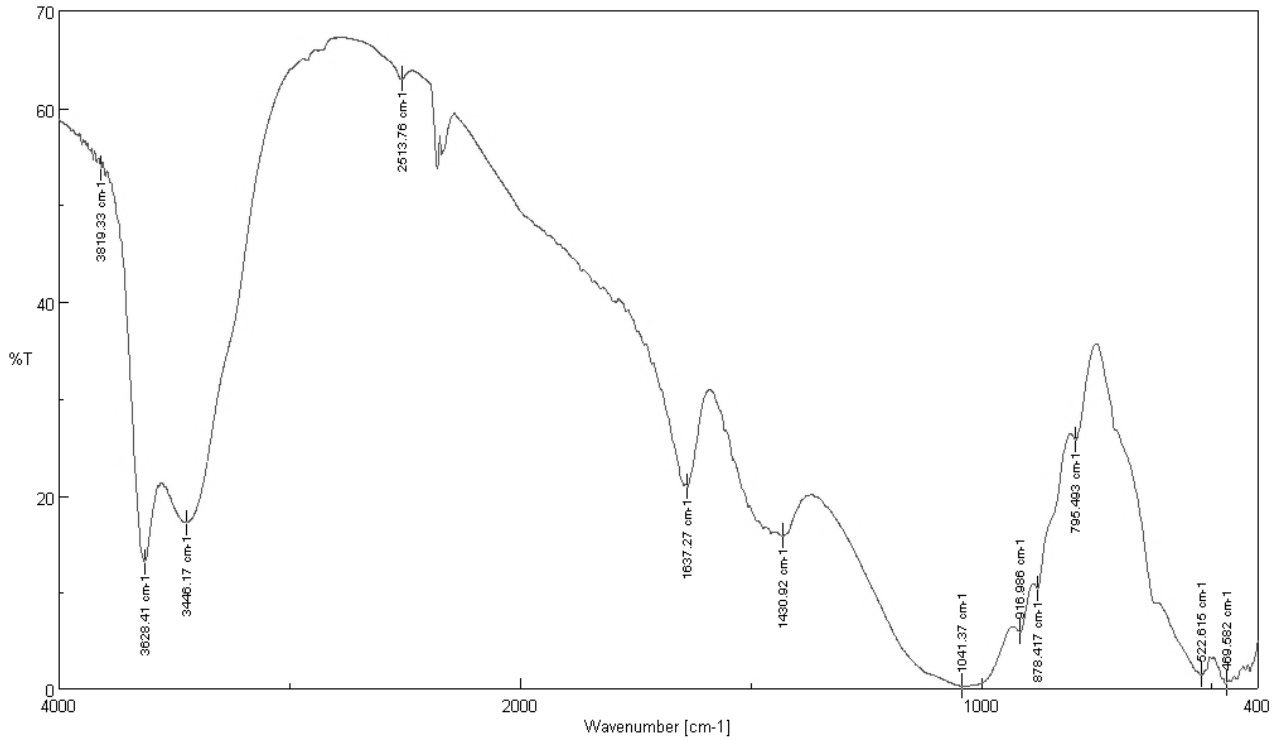




Results - FTIR spectra of bentonite

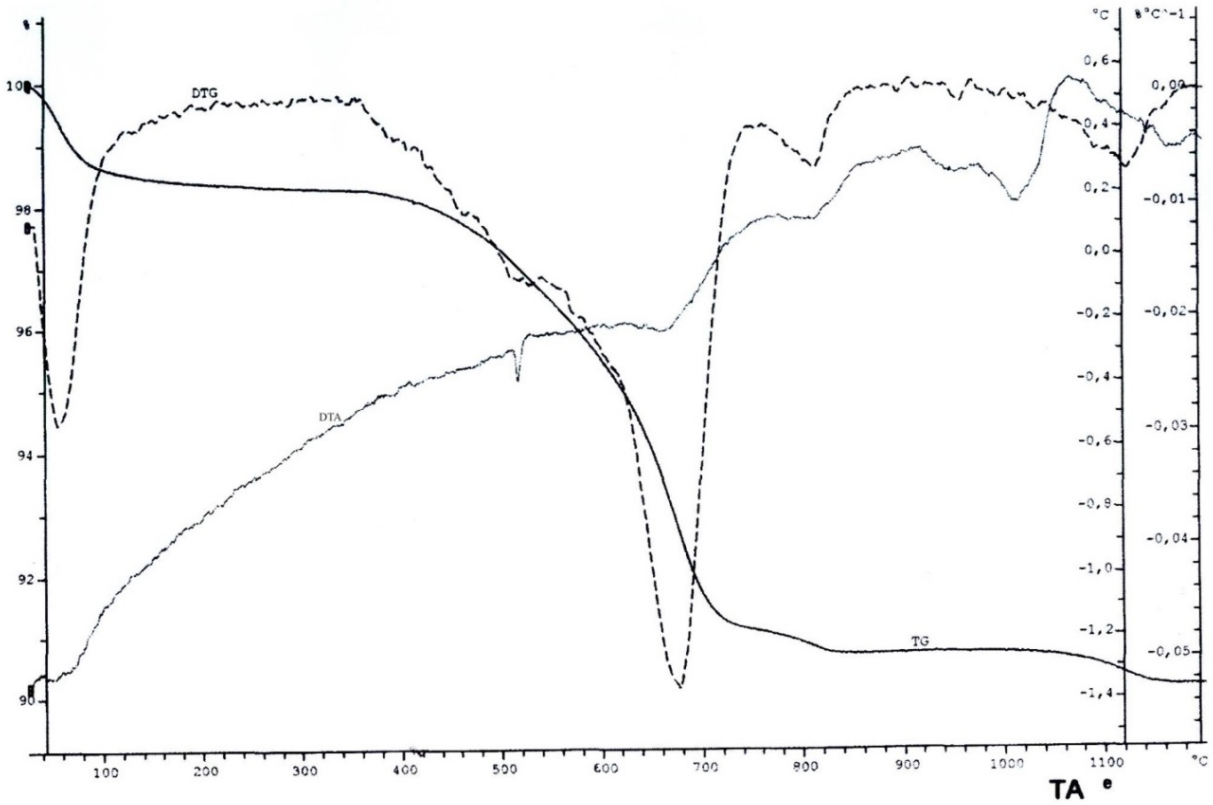
- The vibration given at 917 cm^{-1} refers to the Al^{vi}-OH-Al^{vi} bond and corresponds to pure montmorillonite

- wide vibration at 3446 cm^{-1}, and the sharp vibration at 1637 cm^{-1} are attributed to the adsorbed water



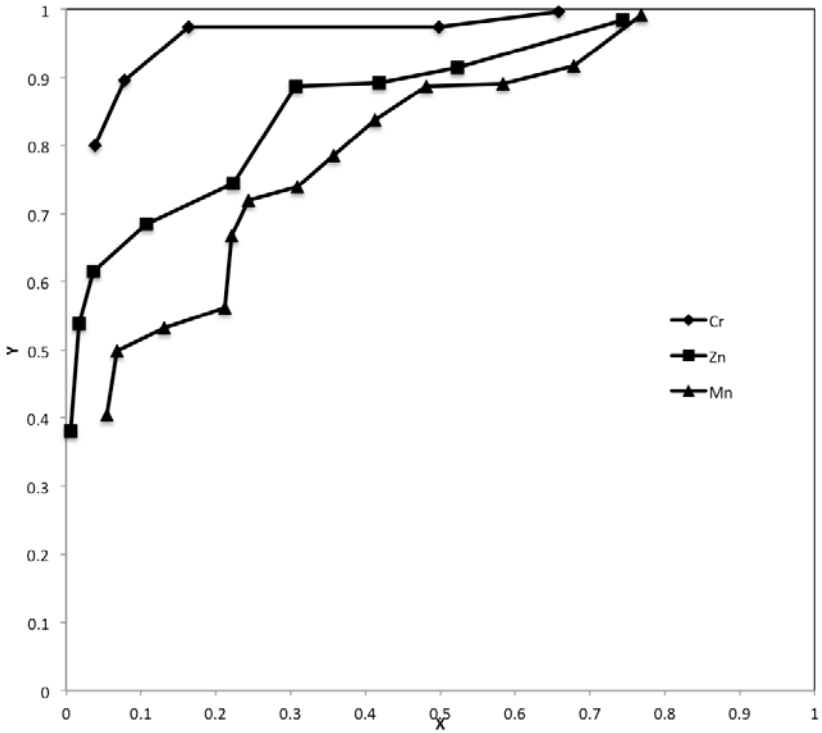
Results : Thermogravimetric analysis of bentonite

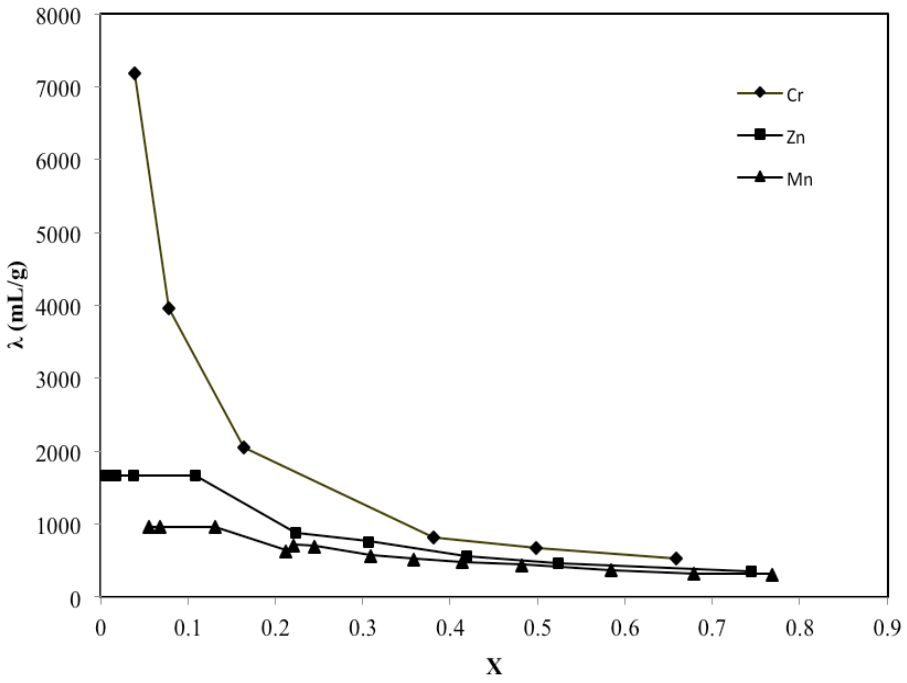
- endothermic peak is observed between 100-400°C, which is the result of dehydration
- endothermic peak which results from dehydroxylation and the exothermic peak which results from recrystallization are observed at 600-800°C



Results

- all isotherms are favorable following the order Cr>Zn>Mn.
- Higher atomic weight and ionic radius, give smaller hydrated radius, which effects significantly in increasing capacity values





Results

MELs of natural bentonite for the three metals studied are presented.

The selectivity series deduced from MEL values follows the order **Cr>Zn>Mn** and is the same compared to the equilibrium isotherms

Minerals Maximum exchange level (MEL)

Metal	meq/g	mg/g
Zn	2,61	85.23
Mn	2,34	64.17
Cr	3,40	58.90

Sorption Isothemrs

- For the purposes of simplified equilibrium modeling in adsorption and ion exchange systems Langmuir equilibrium equation is used

$$\frac{q_e}{Q_M} = \frac{K \cdot C_e}{1 + K \cdot C_e} \Leftrightarrow \frac{1}{q_e} = \frac{1}{Q_M \cdot K} \cdot \frac{1}{C_e} + \frac{1}{Q_M}$$

- Freundlich isotherm equation is also frequently used, especially in liquid-phase systems

$$\frac{q_e}{Q_M} = k \cdot C_e^{Fr} \Leftrightarrow q_e = K_F \cdot C_e^{Fr} \Leftrightarrow \ln q_e = Fr \cdot \ln C_e + \ln K_F$$

Results

- Langmuir isotherm fits data better for Cr, while
- Freundlich seems superior for Zn and Mn.
- Is interesting to note that the ultimate sorptive capacity as estimated by Langmuir isotherm is very close to the MEL value for Cr and Mn and not far for Zn

Models fit and constants

Metal	Concentration (mg/l)	Langmuir			Freundlich		
		Q_M (mg/g)	K (l/mg)	R^2	Fr	K_F	R^2
Cr	172	59.52	0.59	0.98	0.0678	43.28	0.82
Zn	327	71.43	0.39	0.92	0.18	31.1	0.97
Mn	275	60.24	0.05	0.88	0.32	11.29	0.95

Conclusions

- Ion exchange equilibria is examined by use of batch equilibrium isotherms and distribution coefficients for three metals (Zn^{2+}, Cr^{3+} and Mn^{2+}) on natural bentonite.
- All isotherms are favorable.
- Selectivity series derived from distribution coefficients is $Cr^{3+}>Zn^{2+}>Mn^{2+}$ and is the same for maximum exchange level experiments.
- The Langmuir and Freundlich models were applied to describe the equilibrium isotherms for the metal ion uptake.
- According to the results Langmuir isotherm fits data better for Cr, while Freundlich seems superior for Zn and Mn.

Thank you for your attention!!!

V.J. Inglezakis

e-mail: vasileios.inglezakis@nu.edu.kz

Nazarbayev University

Astana, Kazakhstan

IWWATV Industrial Waste & Wastewater Treatment & Valorisation

International Conference

Industrial Waste & Wastewater Treatment & Valorisation: 21-23 May 2015, President Hotel, Athens