DUDAR COAL – NOVEL APPROACHES FOR UTILISATION

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TEKH NATURAL RESOURCES SPECIAL COLLEGE
OUR CHANGING CLIMATE PROJECT

Towards zero carbon emission – new trends in coal application and organic waste Management

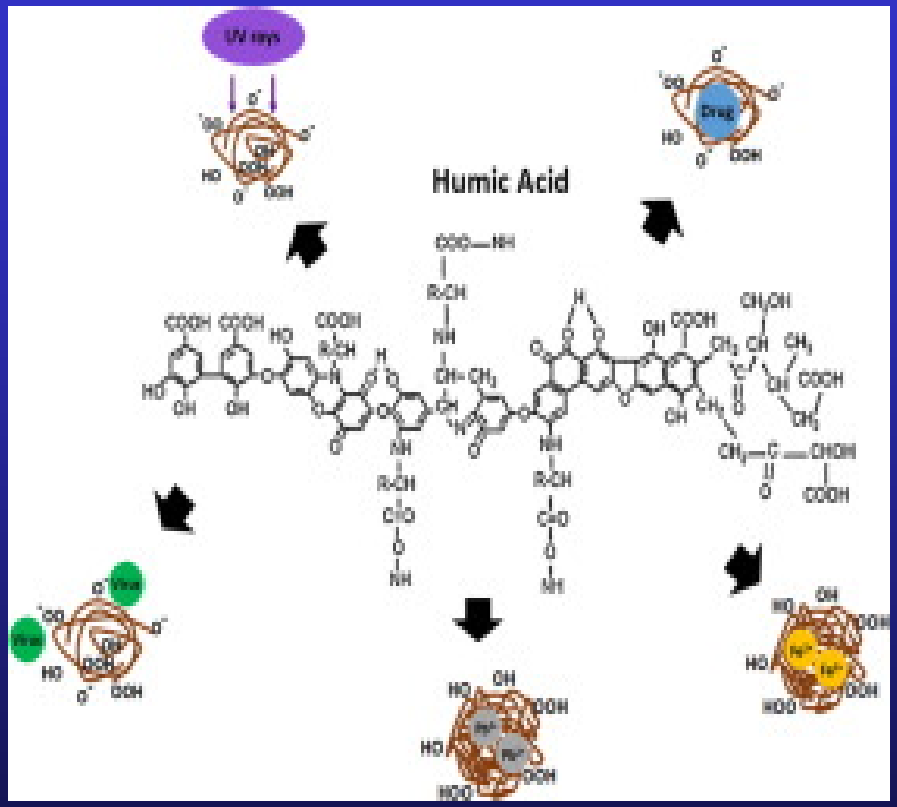
Siófok, Hungary, 12th – 14th May 2022

Introduction

- **Novel utilization of sub-bituminous coal: planned to be used in sewage sludge treatment as adsorbents**
- **Superfast aerobic stabilization of sewage sludge being investigated at Institute of Raw Material Preparation and Environmental Processing of the University of Miskolc**
- **Adsorption of the water-soluble compounds on the coal surface is a part of this stabilization process**
- **Before the stabilization process, it was important to determine the adsorption properties of the additive**
- **Heavy metals can be suitable for determining adsorption properties since they are pollutants and they can be found in sewage sludge, also in dissolved (ionic) form**

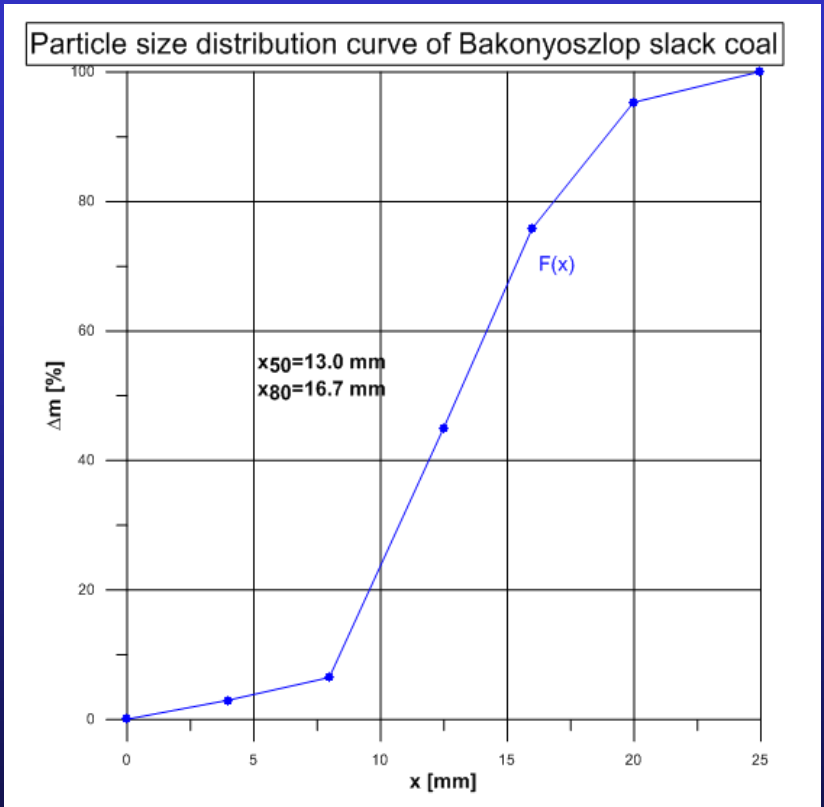
Humic acid content and adsorption

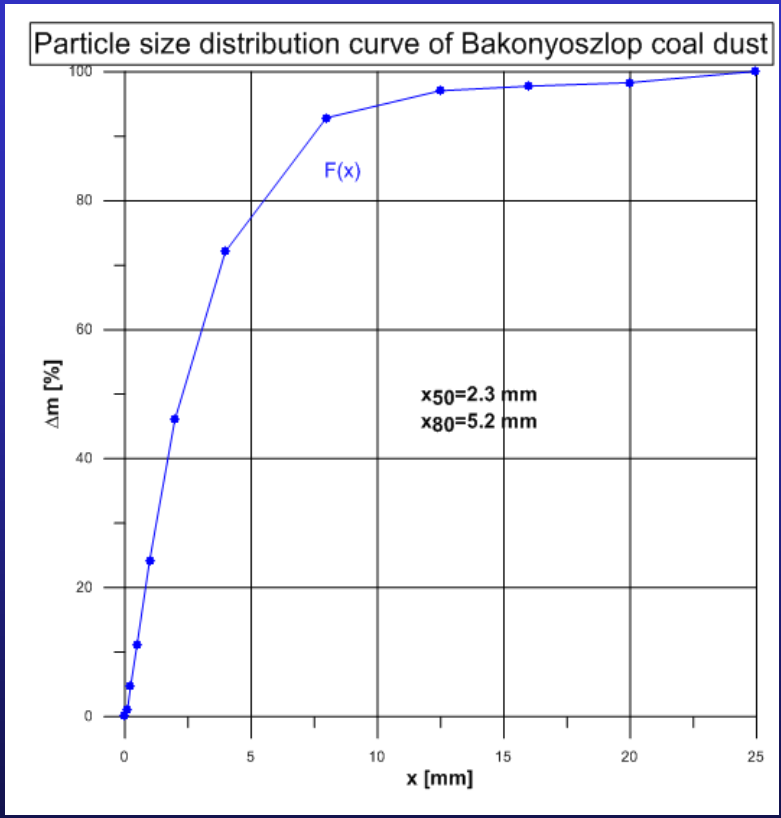
- Adsorption properties of the coal mainly depend on its oxygen bearing functional groups (-OH, -CHO, C=O, -COOH)
- Structure of the humic acid: contains -OH, -COOH, -NH, phenolic –OH groups
- Good adsorption capacity can be expected from the Bakonyoszlop / Dudar coal (60 m/m % humic acid content was reported .)
- Humic acid is a very valuable constituent in further utilization of the treated sewage sludge
- Investigation of the adsorption capacity: via determining and plotting adsorption isotherms



Characterization of the coal

- Two types of Bakonyoszlop coal: slack coal and coal dust





Four different particle size intervals were selected: 12.5-20 mm slack coal, 4-12.5 mm slack coal, 8-12.5 mm coal dust, <8 mm coal dust

Characterization of the coal

Slack coal (12.5-20 mm)

Slack coal (4-12.5 mm)

Coal dust (8-12.5 mm)

Coal dust (<8 mm)

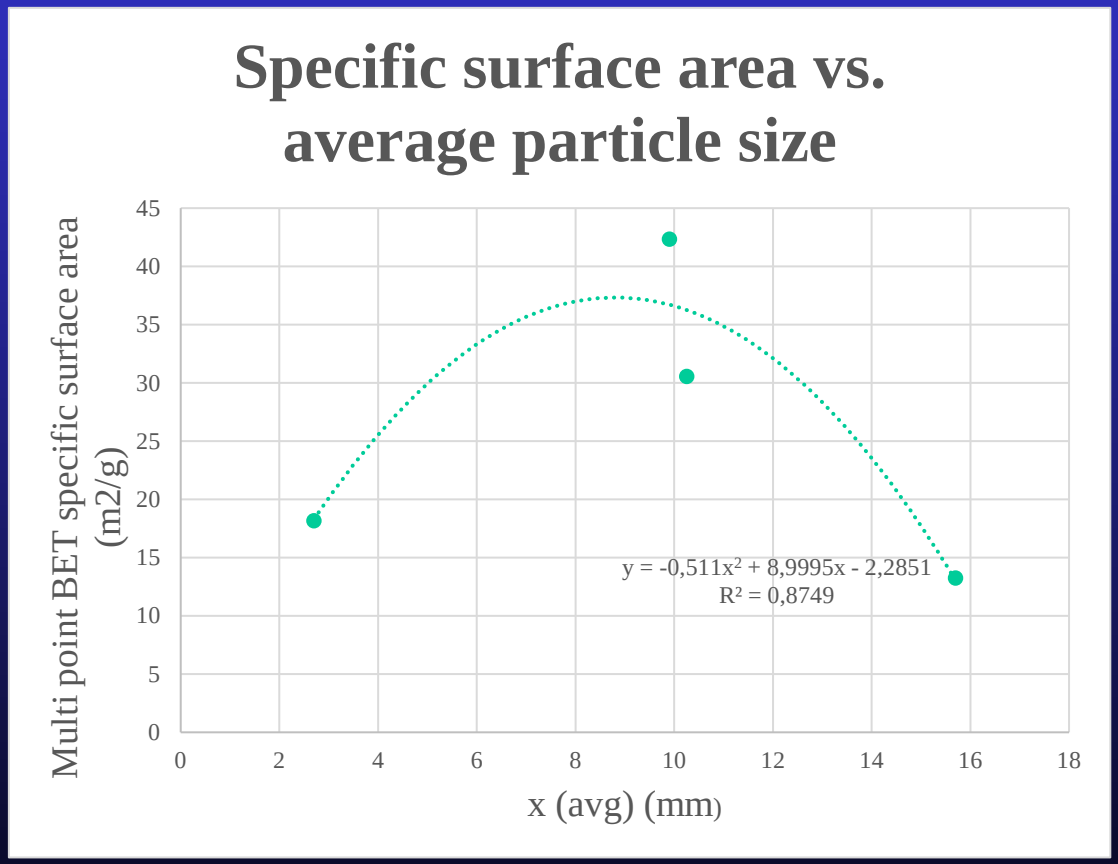
Characterization of the coal

Particle size of the coal	Moisture content (%)	Ash content (%)	
		dry	wet
Slack 12.5-20 mm	19.91	11.34	9.08
Slack 4-12.5 mm	22.33	8.57	6.66
Dust 8-12.5 mm	20.33	14.83	11.82
Dust <8 mm	20.48	19.77	15.72

Particle size of the coal	Single point BET	Multi point BET	Langmuir
	m^2/g	m^2/g	m^2/g
Slack 12.5-20 mm	12.5950	13.2517	18.4102
Slack 4-12.5 mm	39.9550	42.3417	59.5620
Dust 8-12.5 mm	29.0268	30.5753	42.8981
Dust <8 mm	17.1196	18.1722	25.4592

Characterizazion of the coal

- **The relationship between specific surface and average particle size is ambivalent, probably due to the high ash-forming mineral content of the finest fraction**



Adsorption measurements

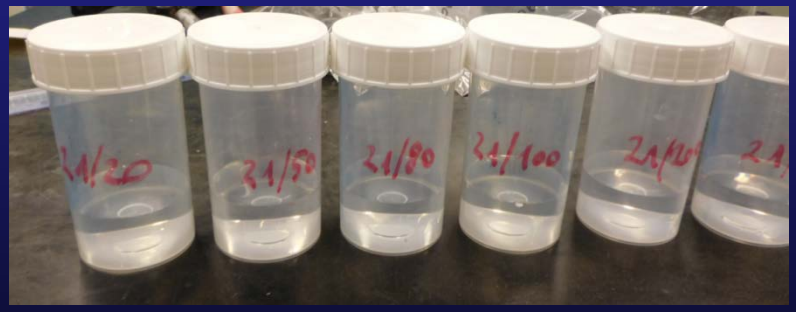
- Batch experiments until the adsorption equilibrium is reached at different heavy metal concentrations
- S:L = 1:10 or 1:40 m/m (2.5-10 g adsorbent + 100 g dist. water)
- Adjustment of pH to 5.0-5.2 (adsorption is strongly pH dependent)
- Heavy metal ions: Pb^{2+} and Cd^{2+} .
- Anions: NO^{3-} és $CH3COO^{-}$.
- Adjusted heavy metal concentrations: 20, 50, 80, 100, 200, 300, 400, 600, 800 és 1000 mg/L.
- Contact time in a Wise Cube shaking machine: 4 h at 150 min^{-1}, temperature was 25ºC.
- After shaking, S/F phase separation with filtering, then preservation of the solution
- Chemical analysis: Philips PU 9100 X atomic absorption spectrometer (Department of Chemistry)

Adsorption measurements

Shaking machine

Filtration

Filtrate samples before chemical analysis



Isotherm calculations

- **The adsorption capacity of the coal (q_{eq}, mmol/g) at equilibrum state was calculated with the following relationship:**

$$q_{eq} = \frac{(c_0 - c_{eq}) \cdot V}{m}$$

c_0: concentration before adsorption in the solution [mmol/L]

c_{eq}: equilibrium metal ion concentration in the solution [mmol/L]

V: volume of the solution [L]

m: weight of the adsorbent [g]

q_{eq}-c_{eq} measurement points → constants of different adsorption isotherms can be determined

Tested models: Tóth, Langmuir and Freundlich adsorption isotherms

Regression and correlation analysis

Isotherm calculations

Isotherms: suitable to describe adsorption from liquid phase.

Most frequently used isotherms (also used by us): Langmuir-isotherm, Tóth-isotherm, Freundlich-isotherm.

<u>Langmuir isotherm:</u>

$$q_{eq} = q_{max} \frac{c_{eq}}{b + c_{eq}}$$

Two constants: q_{max} (maximum adsorption capacity) and b (corresponds to $1/K_L$, which is the equilibrium constant of the adsorption-desorption process)

Presumes monolayer adsorption, a definite number of equivalent adsorption sites, reversible adsorption.

Isotherm calculations

Tóth isotherm:

$$q_{eq} = \frac{q_s c_{eq}}{(b_t + {c_{eq}}^t)^{\frac{1}{t}}} \quad , \qquad t \neq 0$$

Three constants, maximum adsorption capacity, b=1/K_L and t Tóth isotherm constant, the so-called heterogenity constant;

Freundlich isotherm:

$$q_{eq} = K_F \cdot {c_{eq}}^n$$

Entirely empiric (unlike the other two isotherms). Two constants: maximum capacity and adsorption exponent.

Isotherm calculations

Aim: to select one general isotherm for the evaluation of our measurement results

The decision was made by considering:

- **Which isotherm describes the physico-chemical process of the adsorption? (physical content of the constants, interpretation of the stages of the isotherm)**
- **Which one fits the best on the measurement points (correlation coefficient, correlation index, regression coefficients were calculated and compared)**

Based on these aspects:

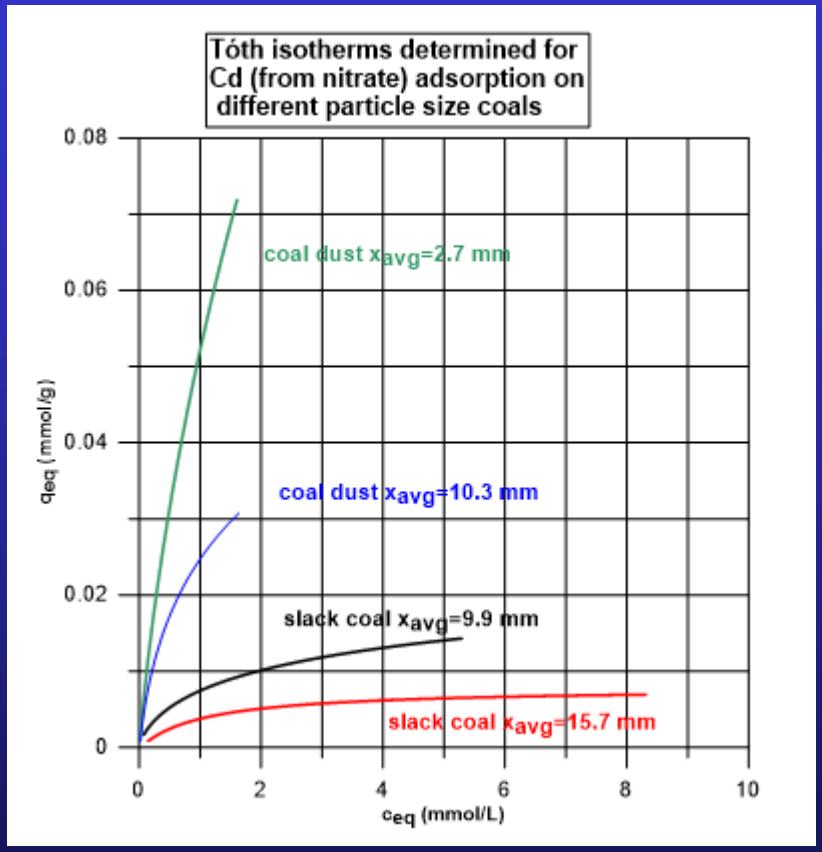
1. **Tóth**
2. **Freundlich**
3. **Langmuir**

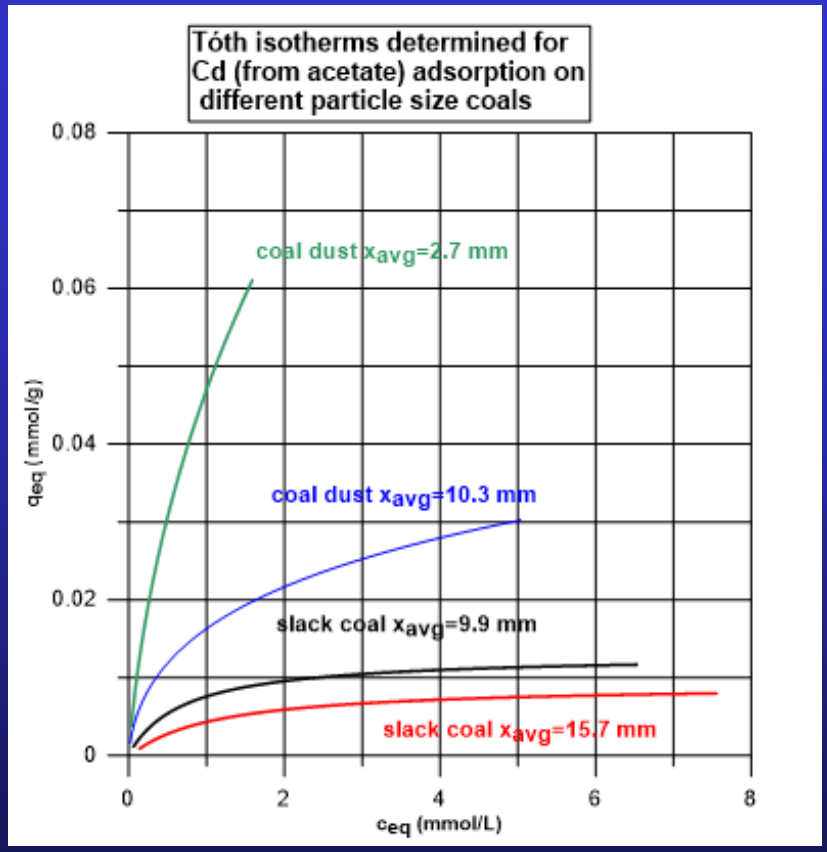
Isotherm calculations

Coal	Cation	Anion	x(avg)	Regr. coeff			Corr. factor			Corr. index		
			mm	Lang.	Freund.	Tóth	Lang.	Freund.	Tóth	Lang.	Freund.	Tóth
slack	Cd^{2+}	acetate	0.25-2	**0.9877**	0.9837	**0.9872**	**0.9930**	0.9908	**0.9926**	**0.9929**	0.9900	**0.9926**
dust	Cd^{2+}	acetate	0.25-2	0.9863	*0.9926*	**0.9980**	0.9942	*0.9961*	**0.9989**	0.9926	*0.9954*	**0.9988**
slack	Cd^{2+}	acetate	<0.25	*0.9681*	0.9568	**0.9728**	*0.9807*	0.8733	**0.9828**	*0.9805*	0.9686	**0.9822**
dust	Cd^{2+}	acetate	<0.25	0.9858	*0.9909*	**0.9969**	0.9937	*0.9952*	**0.9982**	0.9924	*0.9944*	**0.9982**
slack	Pb^{2+}	acetate	0.25-2	*0.9745*	0.9187	**0.9790**	*0.9807*	0.9189	**0.9881**	*0.9220*	0.5746	**0.9763**
dust	Pb^{2+}	acetate	0.25-2	*0.9557*	0.9209	**0.9810**	*0.9774*	0.9549	**0.9918**	*0.9670*	0.9385	**0.9867**
slack	Pb^{2+}	acetate	<0.25	*0.9741*	0.9698	**0.9886**	*0.9859*	0.9833	**0.9933**	*0.9854*	0.9805	**0.9931**
dust	Pb^{2+}	acetate	<0.25	*0.8182*	0.8083	**0.8292**	*0.8743*	0.8656	**0.8868**	**0.8014**	*0.7931*	0.7691

Coal	Cation	Anion	x(avg)	Regr. coeff			Corr. factor			Corr. index		
			mm	Lang.	Freund.	Tóth	Lang.	Freund.	Tóth	Lang.	Freund.	Tóth
slack	Cd^{2+}	acetate	0.25-2	1	3	1	1	3	1	1	3	1
dust	Cd^{2+}	acetate	0.25-2	3	2	1	3	2	1	3	2	1
slack	Cd^{2+}	acetate	<0.25	2	3	1	2	3	1	2	3	1
dust	Cd^{2+}	acetate	<0.25	3	2	1	3	2	1	3	2	1
slack	Pb^{2+}	acetate	0.25-2	2	3	1	2	3	1	2	3	1
dust	Pb^{2+}	acetate	0.25-2	2	3	1	2	3	1	2	3	1
slack	Pb^{2+}	acetate	<0.25	2	3	1	2	3	1	2	3	1
dust	Pb^{2+}	acetate	<0.25	2	3	1	2	3	1	1	3	3
			SUM	17	22	8	17	22	8	16	22	10

Adsorption isotherms



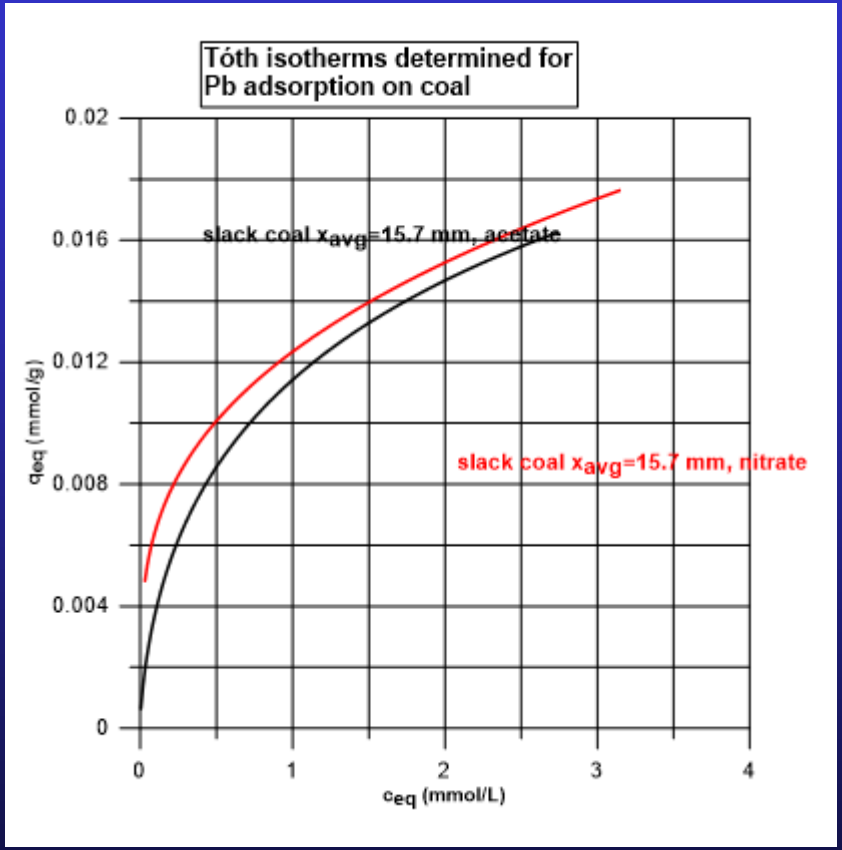


S/L=1:10

Effect of the particle size can be seen

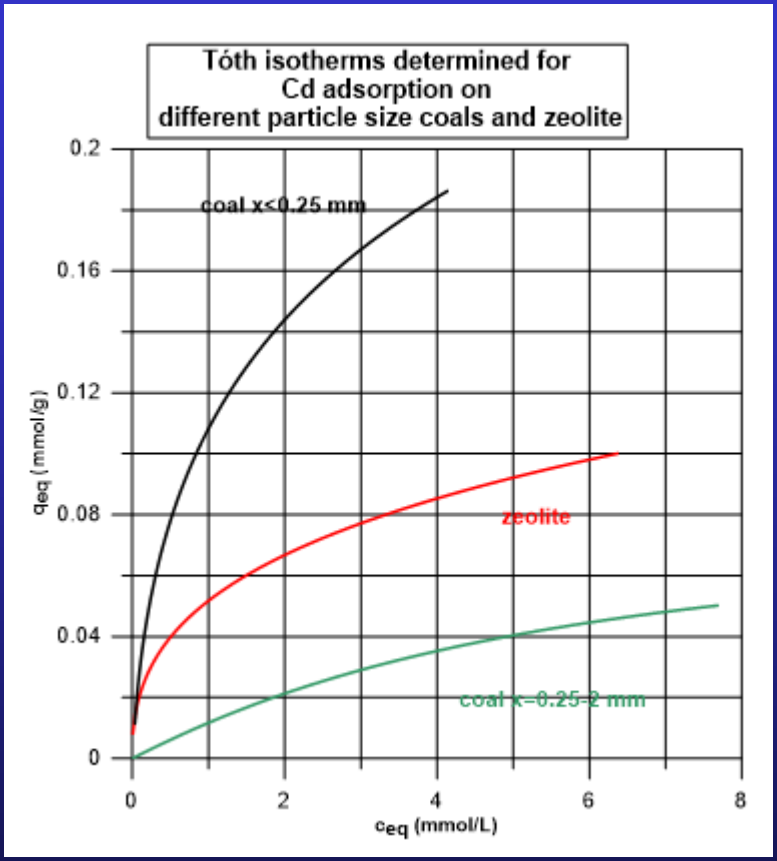
Coal dust > Slack coal (different composition)

Adsorption isotherms



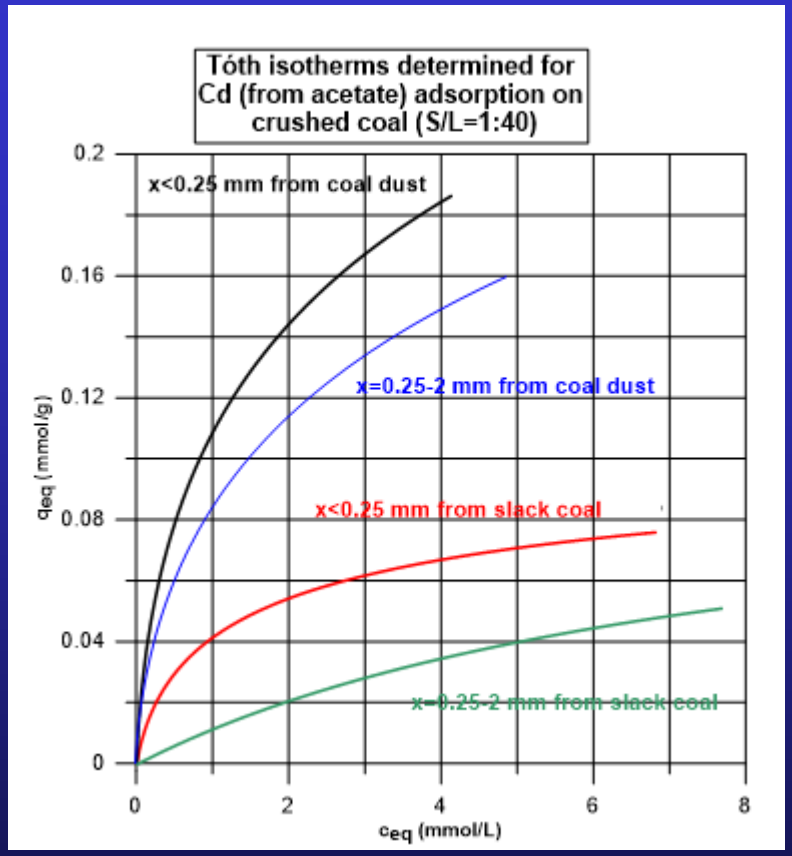
Nitrate anions vs. acetate anions: no significant difference in Pb^{2+} adsorption on coal

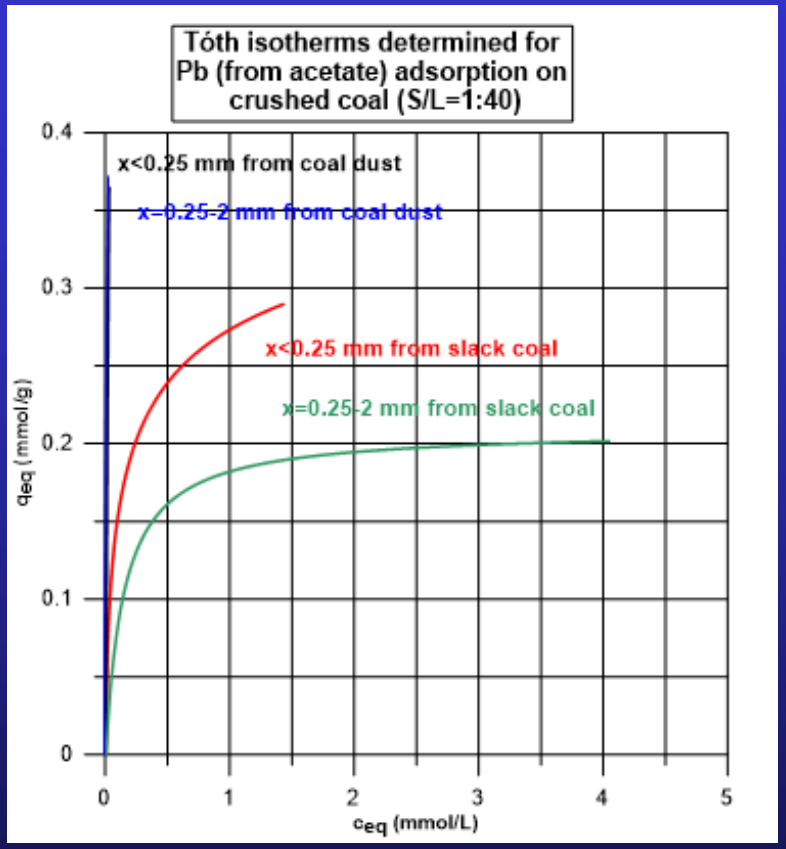
Adsorption isotherms



Comparison of adsorption capacity of coal and zeolite (x_{avg}: 0.3 mm) S/L=1/40, Cd^{2+}, Tóth isotherms

Adsorption isotherms



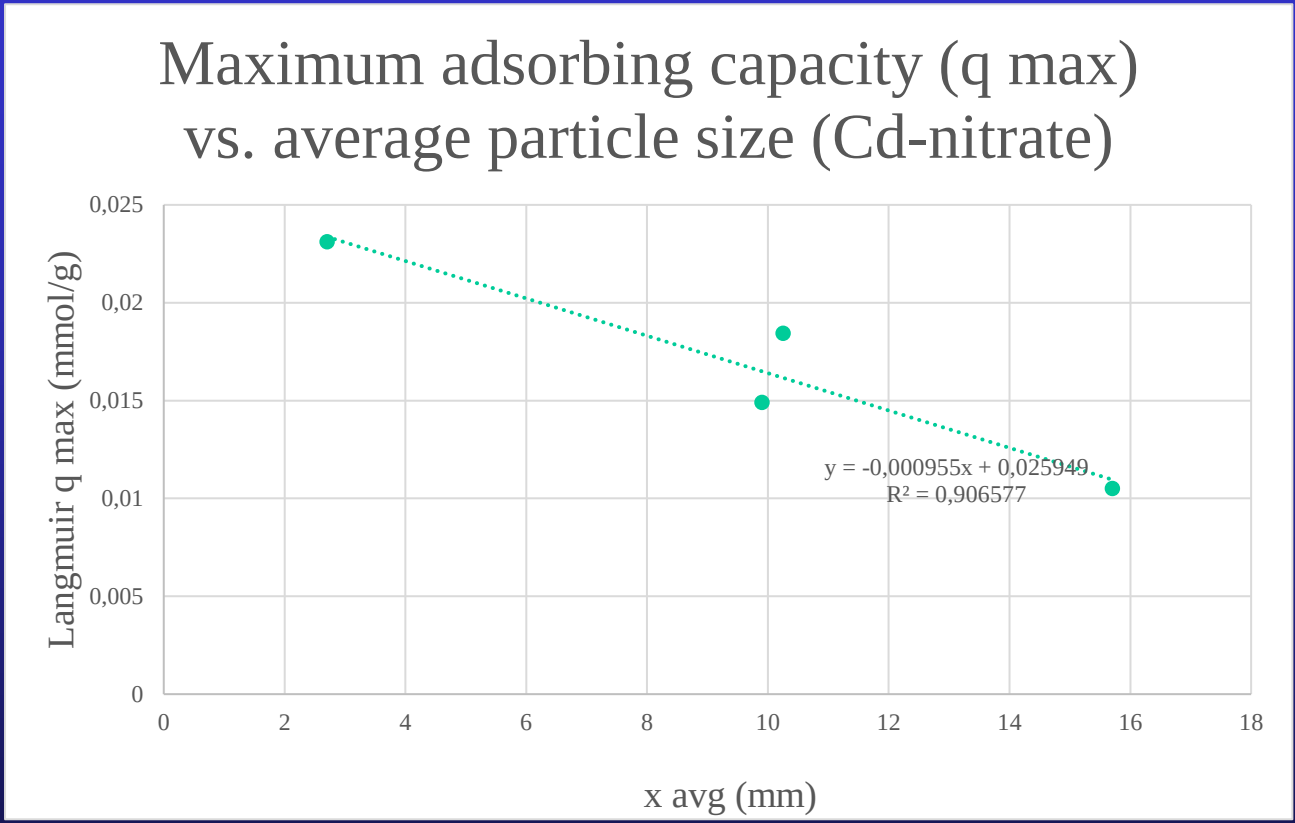


S/L=1:40

Effect of the particle size can be seen

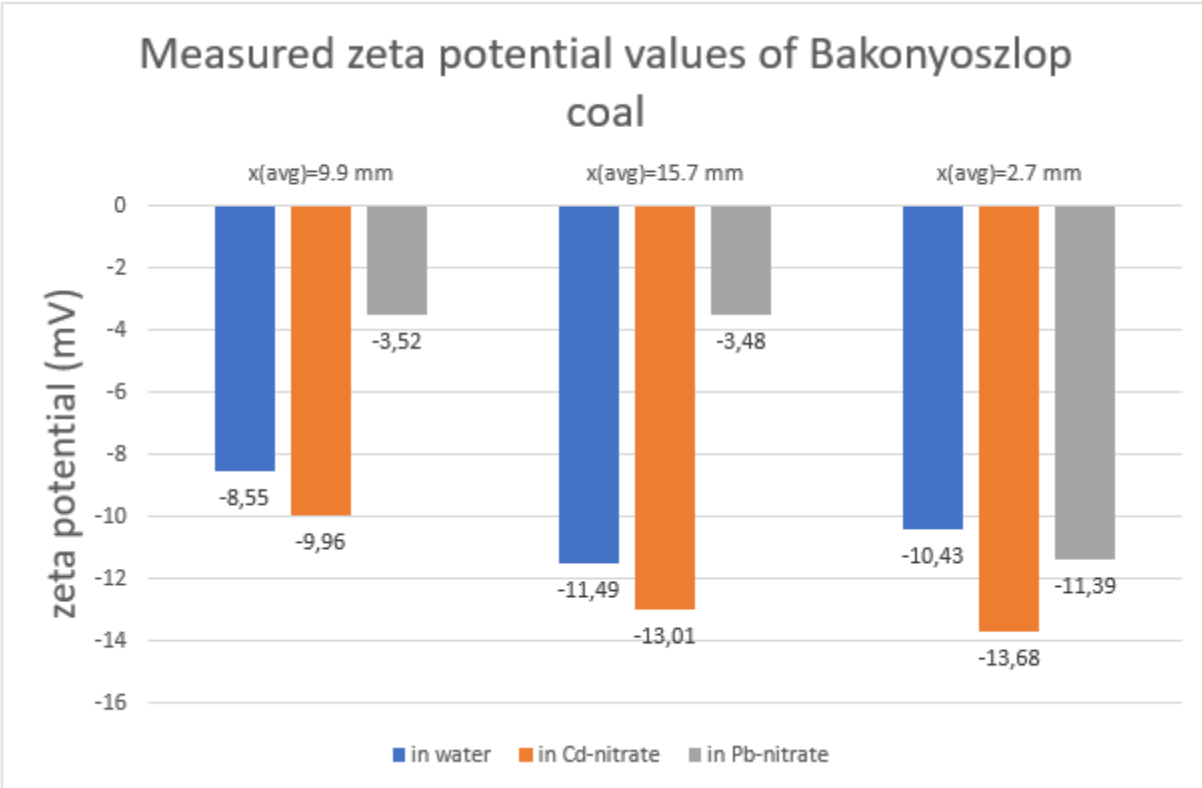
Coal dust > Slack coal (different composition); Pb^{2+}>Cd^{2+}

Adsorption isotherms



Linear relationship within the investigated interval

Zeta potential changes during adsorption



Zeta potential changes during adsorption

Physisorption or specific sorption – can be decided by observing the changes in zeta potential

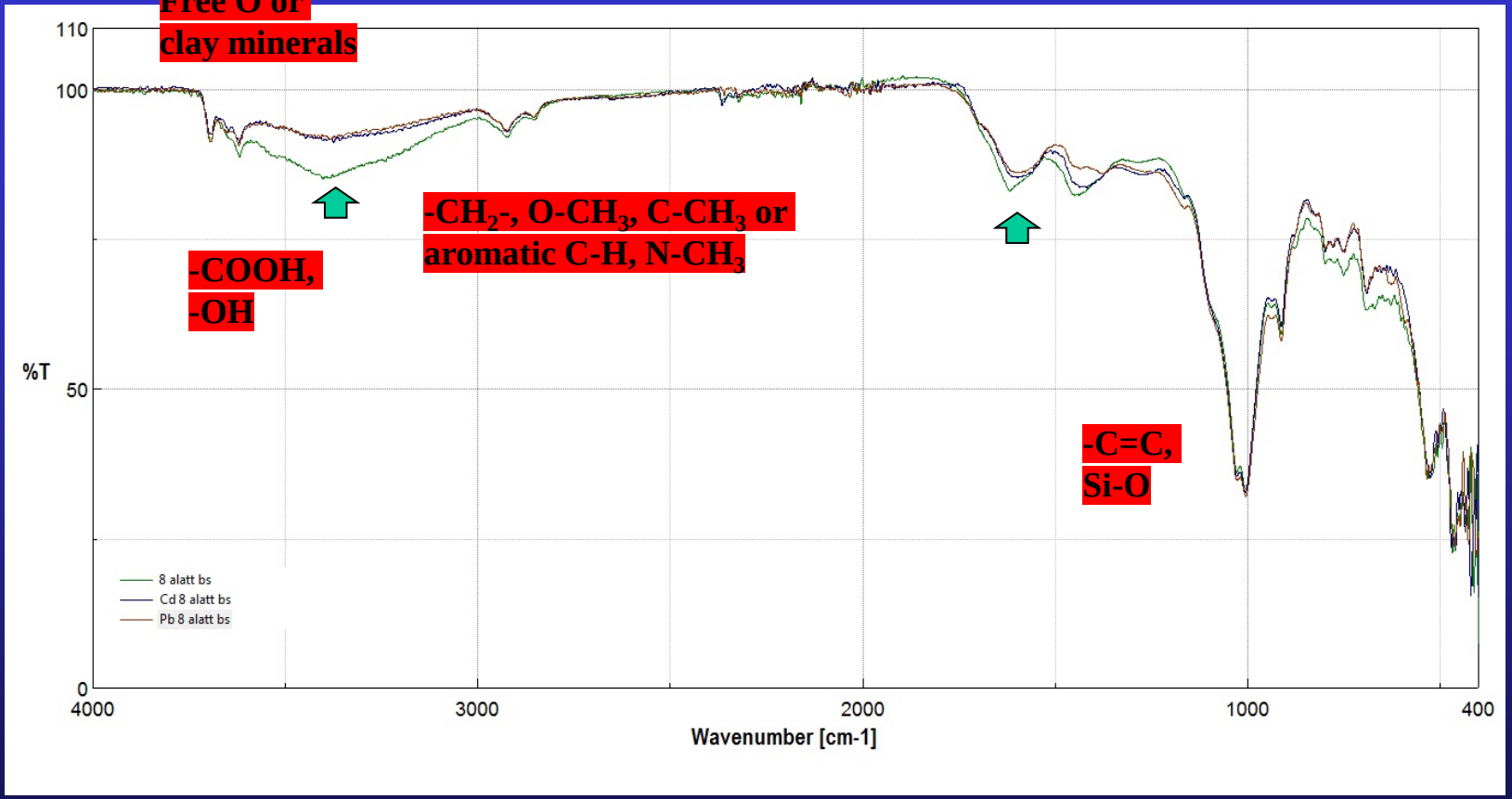
Surface is negatively charged, Pb^{2+} and Cd^{2+} (positive ions) are present:

-if zeta potential becomes less negative as expected, mechanism of adsorption is physisorption (Pb^{2+} adsorption on slack coal)

-if zeta potential becomes more negative, different processes take place, mechanism of adsorption is specific sorption (Cd^{2+} adsorption on all coals, Pb^{2+} adsorption on <8 mm coal dust)

Differences in Pb^{2+} adsorption between coal types!

Changes in FT-IR spectra during adsorption

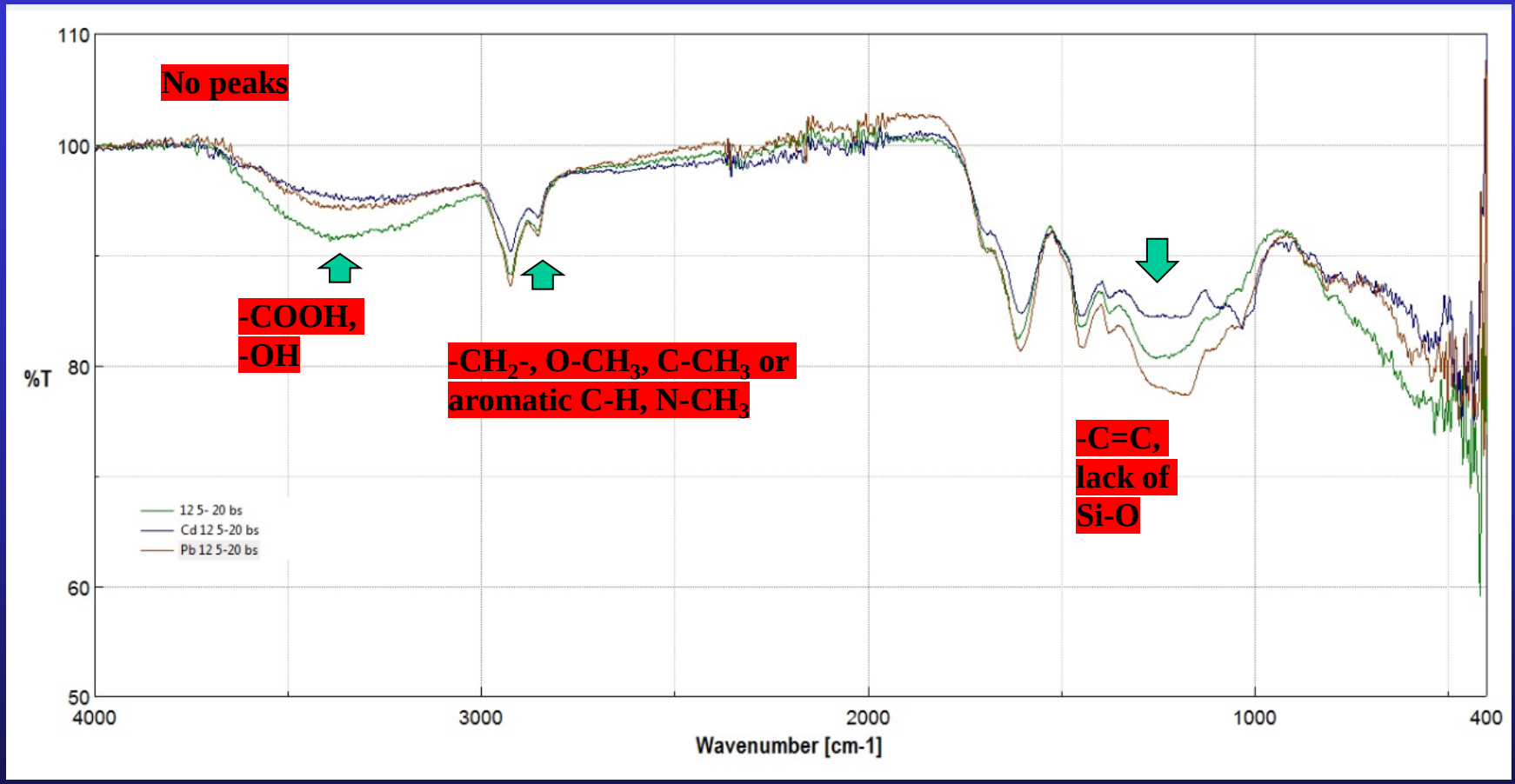


Coal dust x<8 mm – after 4 h contact

Blue: in distilled water, green: in cadmium nitrate, red: in lead nitrate

difference between lead and cadmium adsorption

Changes in FT-IR spectra during adsorption

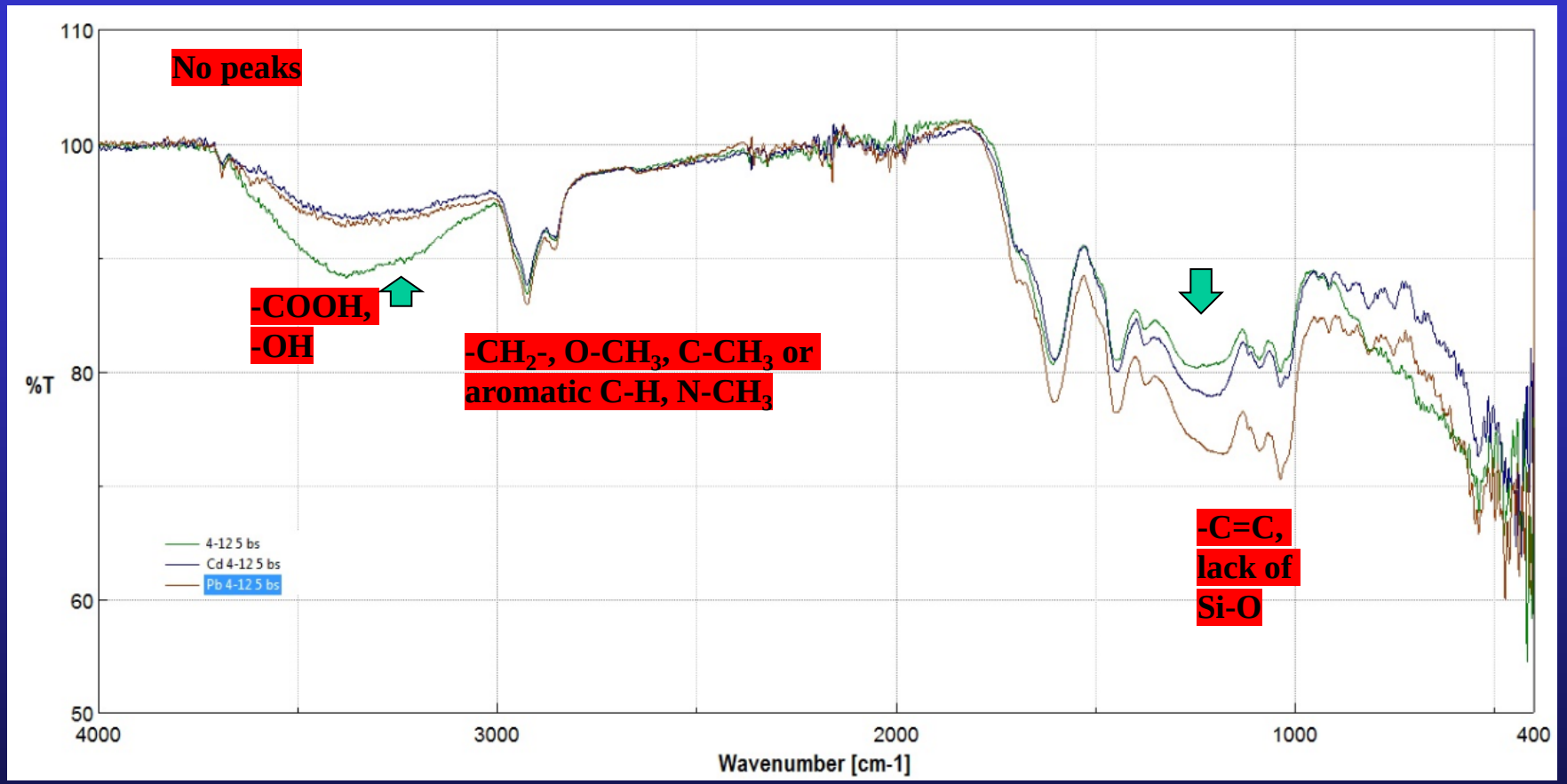


Slack coal 12.5-20 mm – after 4 h contact

Blue: in distilled water, green: in cadmium nitrate, red: in lead nitrate

difference between lead and cadmium adsorption

Changes in FT-IR spectra during adsorption



Slack coal 4.5-12 mm – after 4 h contact

Blue: in distilled water, green: in cadmium nitrate, red: in lead nitrate

difference between lead and cadmium adsorption

Changes in FT-IR spectra during adsorption

As a result of the adsorption, intensity at O-bearing functional group peaks decreases

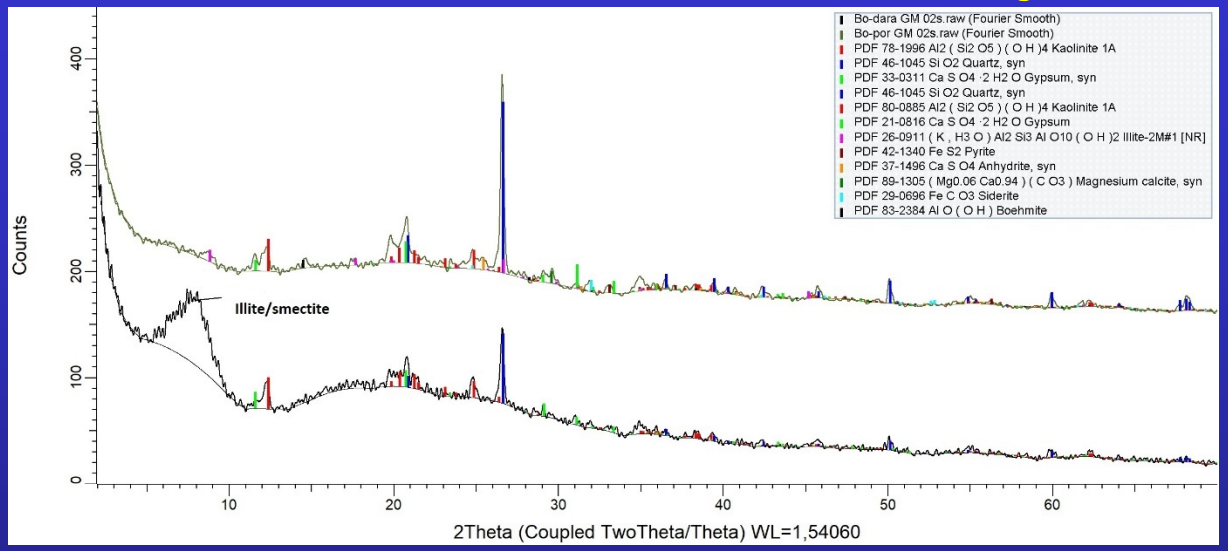
It can be concluded that the FT-IR measurement results correspond with the differences noticed during the zeta potential measurements:

Different types of sorption: <8 mm coal dust vs. two slack coal types (different ash content, Si-O)

There are significant differences between the Cd^{2+} and Pb^{2+} adsorption as well.

(Physisorption vs. specific sorption)

XRD analysis



Different mineral composition can be the reason for different adsorption mechanism, adsorption capacity and differences in FT-IR measurements, zeta potential measurements

PHASE NAME (%)	SLACK
Quartz	3,8
Kaolinit	3,7
Illite/smectite 11A	13,2
Gypsum	1,3
Illite 2M1	9,8
Smectite	11,1
Röntgen amorphous	57,0
TOTAL	100,0

PHASE NAME (%)	DUST
Quartz	9,2
Kaolinit	11,5
Gypsum	1,3
Illite 2M1	15,6
Calcite	1,4
Pyrite	0,6
Siderite	0,4
Boehmite	1,4
Illite/smectite 12A	2,4
Anhydrite	0,9
Röntgen amorphous	55,1
TOTAL	100,0

Higher adsorption capacity

Can be reached by:

- **Crushing the coal**
- **Increasing contact time (e.g. 1 week)**
- **Decreasing the S/L ratio by using less coal**
- **Aiming at reaching higher maximum c_{eq} values by using higher heavy metal concentration solutions**

S/L ratio=1:40, <250 microns: 0.3548 mmol/g Pb^{2+}

S/L ratio=1:100, <250 microns, 1 week treatment (4 hours of shaking every day): 0.481 mmol/g Pb^{2+}, but still at low c_{eq}, estimated c_{eq} by extrapolation: 1.04 mmol/g Pb^{2+}

For Cd^{2+}, values of 0.2 mmol/g can be reached

Comparison with other coals

Difficult to be made, reasons:

- **Adsorption of similar Hungarian coals were investigated by using different metal ions**
- **Particle size was different**
- **pH was different**
- **Coals were pre-treated to improve adsorbing capacity**

Possible solutions:

- **Trying to estimate it by comparing different ion adsorbing capacities (adsorption affinity is known):**

$$Pb > Cr^{3+} > Fe^{2+} > Cu > Zn > Cd > Co > Ni$$

- **Comparing the data with international data.**

Overall, from adsorption data it can be presumed that the Bakonyoszlop coal has a good adsorption capacity related to other Hungarian lower rank coals.

Thank you for your attention!

The experimental work was carried out as a part of „Development of bio raw materials products range with a special regard to the local technology – reseArch on the possibility of utilisation by technological ‚optimisation' GINOP-2.2.1-15-2017-00069 R&D Project.