

# HIGH ENTROPY ALLOWS A BETTER AFFINITY BETWEEN METAL IONS AND ACTIVATED CARBON FIBRES

## VELIKA ENTROPIJA OMOGOČA BOLJŠO AFINITETO MED KOVINSKIMI IONI IN AKTIVIRANIMI OGLJIKOVIMI VLAKNI

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Recent numerical approaches to extracting metal species using carbonaceous materials have de facto stimulated an interest in the field of microextraction, but theoretical observations inspired by randomness changes have been elusive. In this contribution, we present the degree of randomness using Cu (II) and Pb (II). Here, activated carbon fibres were employed as the skeleton adsorbent, providing scientific insights via the aqueous phase. Coupled isotherms of Langmuir and Freundlich were represented to unravel the aforementioned thermodynamics. Findings revealed that the Langmuir isotherm best described the equilibrium state and the trend was in accordance with the energy computation. The maximum microextraction performance was 84.75 mg/g and 102.04 mg/g for Cu (II) and Pb (II), respectively. Under all circumstances, there was a high randomness change as the microextraction performance increased.

**Keywords:** randomness, microextraction, thermodynamics, isotherms

Nedavni numerični pristopi ekstrakcije (izločevanja) kovinskih ionov z uporabo materialov na osnovi ogljika so dejansko povečali interes za področje mikroekstrakcije. Vendar pa rezultati teoretičnih spoznanj, ki temeljijo na ključnih spremembah, še niso povsem jasni. Avtorji v članku predstavljajo stopnjo naključnosti z uporabo Cu(II) in Pb(II) ionov. Kot ogrodje za adsorpcijo so uporabili aktivirana ogljikova vlakna, kar naj bi omogočilo znanstveni vpogled v dogodke potekajoče preko vodne faze. Predstavili so združene Langmuirjeve in Freundlichove izoterme za pojasnitev zgoraj omenjene termodinamike. Ugotovili so, da Langmuirjeva izoterma najboljše opiše ravnotežno stanje, njen trend pa se ujema z energijskimi izračuni. Dosegli so maksimalno mikroekstrakcijo 84,75 mg/g za Cu(II) in 102,04 mg/g za Pb(II) ione. V vseh primerih je prišlo do velikih naključnih sprememb z naraščajočo sposobnostjo mikroekstrakcije.

**Ključne besede:** naključnost, mikroekstrakcija, termodinamika, izoterme

## 1 INTRODUCTION

Gibbs pioneered the concept of randomness with a simple mathematical formalism in the second half of the 19<sup>th</sup> century.<sup>1</sup> Several decades later, Prigogine bridged thermodynamics and kinetics of chemically reacting mixtures in the equilibrium state. In recent years, impressive technological achievements for a better description of the microextraction performance have employed the concept of entropy change ( $\Delta S^\circ$ ), enthalpy change ( $\Delta H^\circ$ ) and the Gibbs standard energy change ( $\Delta G^\circ$ ) to characterise the force irreversibly driving chemical reactions.<sup>2,3</sup> We further abbreviated the  $x$ -change as  $x$  for convenience. Isotherms of Langmuir and Freundlich have led to further observations of the microextraction performance, corresponding to various surface characteristics and the initial dosage of cationic species.<sup>4</sup> On the one hand, the Langmuir isotherm describes the monolayer assuming all adsorption sites to be equally active. Here, the surface is energetically homogeneous due to the

free-energy change at all possible sites. On the other hand, the Freundlich isotherm is valid for heterogeneous surfaces, predicting multilayer adsorption. A myriad of references to date has coupled thermodynamics and isotherms to improve the material design and engineering for a better microextraction performance.<sup>5,6</sup>

In this study, we first set out to do the standard energy computations of metal species on a carbonaceous surface to obtain a deep understanding of microextraction. In doing so, we hypothesised that  $\Delta S^\circ$  and the microextraction performance are in a linear correlation. Our theory corresponds to the Debye-Huckel limiting law where the ion-activity coefficient is the function of the ionic strength at the equilibrium state and the charge carried by metal species,<sup>7</sup> given that an increased value of  $\Delta S^\circ$  at the final stage of ion interaction may reflect the high degree of freedom between the surface moieties and metal species on the carbonaceous surface. For a cross-validation, Langmuir and Freundlich isotherms were employed to explore the surface physiochemistry. Amidst all the growing niches of the microextraction from wastewater or spent catalysts, metal species of Cu (II)

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and Pb (II) were chosen as the interacting ions. These species are also widely used in thermodynamic studies since their alloys form the basis of structural components.<sup>8</sup> As a skeleton adsorbent, activated carbon fibres (ACFs) were examined via an aqueous solution. Compared with the other carbonaceous materials (viz., activated carbons), ACFs exhibit excellent mechanical and physical properties.<sup>9–11</sup> With their fibre forms, they may serve as a decent supporting matrix for selected metal species.<sup>12,13</sup>

## 2 EXPERIMENTAL PART

### 2.1 Preparation of the samples

All the chemicals were of analytical grade and used without further purification (Sigma-Aldrich). Deionised-distilled water (DDW) was used during the experiments. Commercial ACFs with various Brunauer-Emmett-Teller (BET) surface areas were used as adsorbents and the structural features were measured with the Barrett-Joyner-Halenda (BJH) method. These two parameters are defined with Equations (1) and (2), respectively:

$$S_{\text{BET}} = \sigma_m N \left( \frac{w_m}{M_m} \right) \quad (1)$$

$$\ln(p^0/p) = - \left[ \frac{2YV}{RT(r-t)} \right] \quad (2)$$

where  $\sigma_m$  is the surface area of an absorbed molecule of water,  $N$  is Avogadro's number,  $w_m$  is the moisture content due to the monolayer saturation and  $M_m$  is the molar mass of water in the BET equation. In case of the BJH equation,  $Y$  is the surface tension,  $V$  is the molar volume,  $R$  is the gas constant,  $T$  is the temperature in kelvin,  $r$  is the average pore radius and  $t$  is the layer thickness. Sample characteristics were determined with ASAP 2460 (Micromeritics). Here, three commercial ACFs with different carbonisation and activation temperatures were labelled as ACF850, ACF875 and

ACF900 via a CO<sub>2</sub> atmosphere. With an increase in the temperature from 850–900 °C, ACF875 was found to secure the most microporous characteristics among the ACF samples (Table 1). As can be seen in Figure 1, this is in line with the scanning-electron-microscope images observed at an accelerating voltage of 20 kV (S-3000H, Hitachi). The chemical properties of ACF875 also parameterised the most oxygen groups, in order words, carboxylic acids, as listed in Table 2 (EA-1008, Fisons).<sup>13</sup> Typically, surface sites containing oxygen bonding are the main interactors for the microextraction of metal species. Given that, adsorbents with rich surface characteristics could create more ionic species than in the opposite case.

**Table 1:** Physical nature of ACF samples obtained with BET and BJH analyses

Sample	$S_{\text{BET}}$ (m <sup>2</sup> /g)	Micro- pore area (m <sup>2</sup> /g)	External surface area (m <sup>2</sup> /g)	BJH ad- sorption pores (m <sup>2</sup> /g)	BJH desorption pores (m <sup>2</sup> /g)
ACF850	971	893	78	35.5	36.8
ACF875	1443	1246	197	38.2	37.3
ACF900	1026	914	112	36.1	37.0

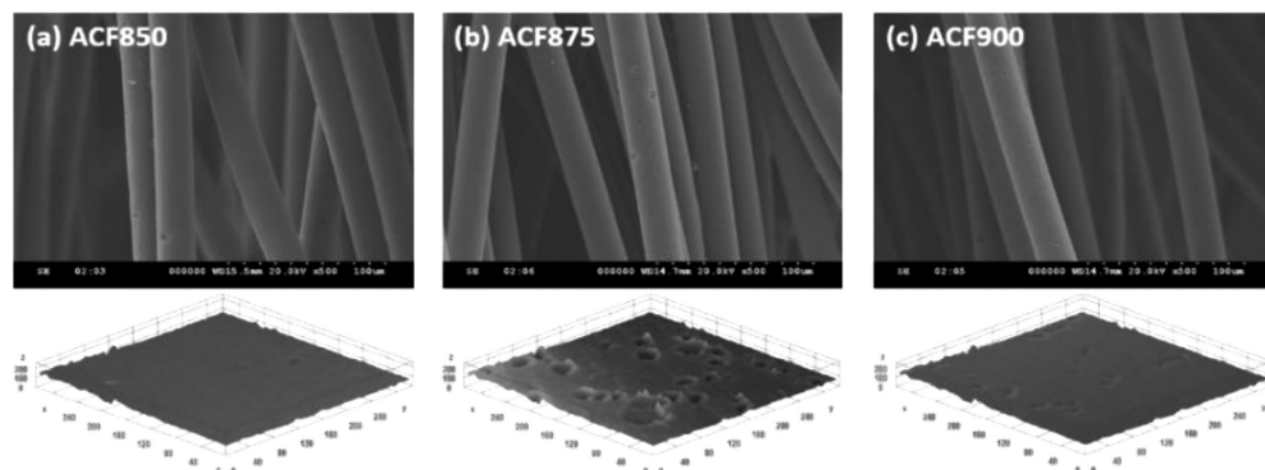
Within the same grid-scale model with a given magnitude of  $\times 10$  K, ACF875 revealed the most porous surface texture among the ACF samples.

**Table 2:** Chemical nature of ACF samples obtained with elemental analyses

Sample	Elemental composition (w/%)			
	C	H	N	O
ACF850	97.45	0.33	0.36	1.82
ACF875	94.54	0.39	0.40	4.67
ACF900	95.50	0.35	0.37	3.78

### 2.2 Modelling

Microextraction-capacity constant  $q$  could be derived with Equation (3):



**Figure 1:** Morphologies of ACF samples observed with a scanning electron microscope

$$q = \frac{(C_o - C_e)V}{W} \quad (3)$$

where  $C_o$  (mg/g) is the initial concentration,  $C_e$  (mg/g) is the plateau equilibrium concentration,  $V$  is the volume of the metal-containing solution, and  $W$  is the weight of each ACF sample. Thermodynamic parameters  $\Delta H^\circ$  and  $\Delta S^\circ$  were calculated using Equation (4):

$$\ln K_L = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (4)$$

where  $K_L$  is the equilibrium constant and the rest is explained above. Thereafter,  $\Delta G^\circ$  can be obtained with Equation (5):

$$(5)$$

The equilibrium microextraction capacity of the ACF samples was fitted using the nonlinear isotherms of Langmuir and Freundlich. The former could be addressed as Equation (6):

$$q_e = \frac{Q_o K_L C_e}{(1 + K_L C_e)} \quad (6)$$

where  $K_L$  is the Langmuir constant. The Freundlich constant  $K_F$  could be obtained with Equation (7):

$$q_e = K_F C_e^{1/n} \quad (7)$$

where  $n$  is the Freundlich exponential coefficient.

## 2.3 Methodology

Microextraction of metal species for thermodynamics and isotherms was carried out in a batch as follows. First, different concentrations of Cu (II) and Pb (II) were prepared using DDW. The initial pH of the solution was adjusted to 5.5 to achieve the highest efficiency. A small amount (100 mg) of adsorbents was added to each flask; then flasks were sealed with silicon caps to prevent further evaporation and shaken at 120 min<sup>-1</sup> in a rotary shaking incubator with a designated temperature and time frame. Inductively coupled plasma optical emission spectroscopy was employed to analyse the microextraction characteristics of the metal species (Optima 5300DV, PerkinElmer).

## 3 RESULTS AND DISCUSSION

### 3.1 Microextraction thermodynamics

The calculated values of the thermodynamic parameters are listed in **Table 3**. The positive value of  $\Delta H^\circ$  can be described with the theory of endothermic nature of a microextraction process. This feature may be an indication of the occurrence of monolayer adsorption. The value is consistent with the fact that microextraction onto carbonaceous materials is usually an ion-exchange process between metal ions and oxygen groups.<sup>14,15</sup> The positive value of  $\Delta S^\circ$  reflects an increase in the randomness at the solid-solution interface. There are various explanations of the randomness increment. One evident approach is that structural changes of ACF samples treated by different temperatures take place as a result of interactions of metal species with oxygen groups on the carbonaceous surface. Elsewhere, we find the suggestion that the extra translational  $\Delta S^\circ$  accumulated due to the solvent molecules earlier absorbed by ACF samples and further displaced by the adsorbate species. The above explanations indicate an overall negative change of  $\Delta G^\circ$ .

Many theorists agreed that  $\Delta G^\circ$  values in the -20 kJ/mol to 0 kJ/mol range correspond to the physisorption, indicating an electrostatic interaction between the adsorption sites and the interacting ions.<sup>16</sup> In case of the chemisorption within the -80 kJ/mol to -400 kJ/mol range, the microextraction involves sharing or transferring of the charge between the adsorption sites and interacting ions to form a coordinate bond. As  $\Delta G^\circ$  of the ACF samples in this study showed a negative linear correlation from -2.45 kJ/mol to -5.64 kJ/mol and -4.23 kJ/mol to -7.47 kJ/mol for Cu (II) and Pb (II), respectively, it can be concluded that a spontaneous type of physisorption dominates the microextraction mechanism.

### 3.2 Microextraction isotherms

The linearized forms of the Langmuir and Freundlich isotherms and the corresponding constants are shown in **Figure 2** and **Table 4**. The analysis of  $R^2$  revealed a reasonable fit of the empirical data on both isotherms, while the Langmuir isotherm (0.9885–0.9953) seemed more favourable compared to the Freundlich isotherm (0.9835–0.9914) in all cases. The maximum microextraction  $q_{\max}$  was estimated to be 84.75 mg/g and 102.04 mg/g for Cu (II) and Pb (II), respectively. In all cases, ACF875 secured an outstanding microextraction

**Table 3:** Thermodynamic constants of microextraction for various ACF samples

Classification	Temperature (°C)	$\Delta G^\circ$	$\Delta H^\circ$	$\Delta S^\circ$	
Cu (II)	ACF850	25 / 35 / 45	-2.45 / -2.87 / -3.38	4.52	23.24
	ACF875	25 / 35 / 45	-4.25 / -4.91 / -5.64	6.11	34.61
	ACF900	25 / 35 / 45	-3.51 / -4.06 / -4.58	4.51	26.83
Pb (II)	ACF850	25 / 35 / 45	-4.23 / -4.88 / -5.60	6.03	34.28
	ACF875	25 / 35 / 45	-5.63 / -6.49 / -7.47	8.06	45.73
	ACF900	25 / 35 / 45	-4.85 / -5.55 / -6.29	5.88	35.89



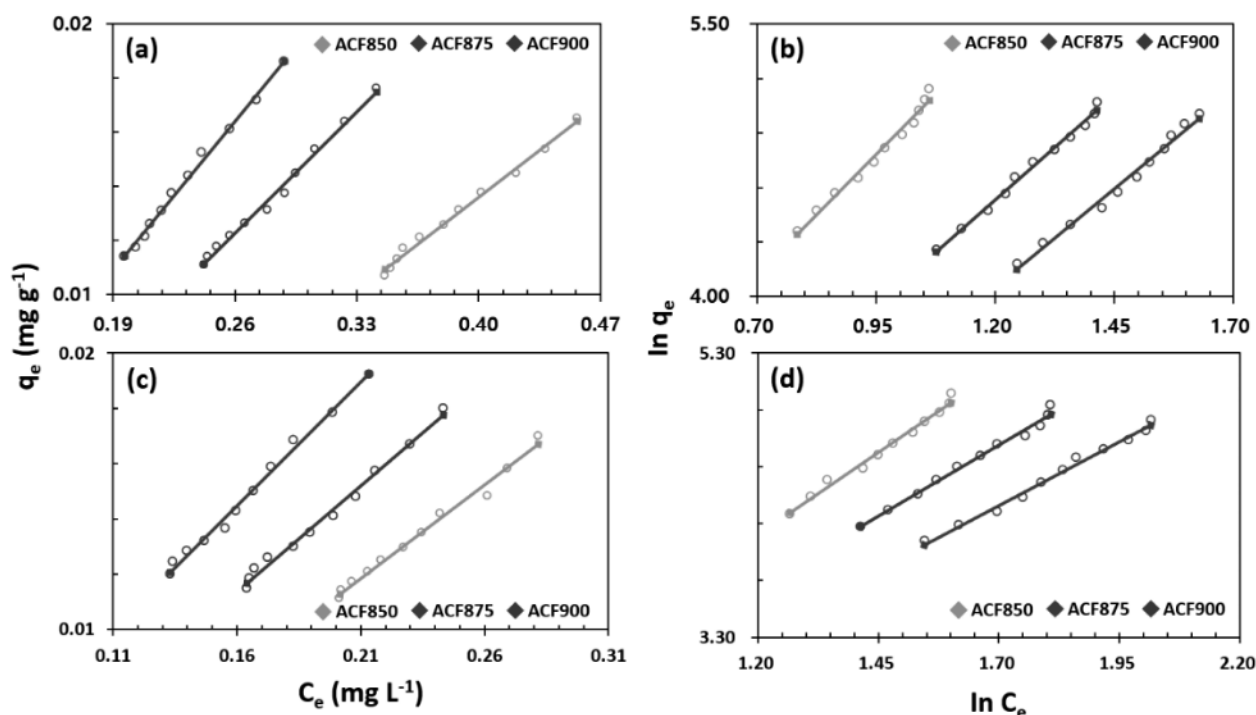


Figure 2: Linearised isotherms: a) Langmuir-Cu (II), b) Freundlich-Cu (II), c) Langmuir-Pb (II), d) Freundlich-Pb (II)

performance compared to the other ACF samples. The metal affinity with the ACF samples was in the order of Pb (II) > Cu (II). To quantify the maximum microextraction performance for a further assumption, we employed the  $q_{\max}$  values from the Langmuir isotherm. We used these values to investigate the correlation between  $\Delta S^\circ$  and  $q_{\max}$  by observing the degree of an entropically favourable state.

Figure 2 shows a comparison of the isotherms for the microextraction of metal species onto various ACF samples. Each ACF sample of 100 mg was tested at 25 °C, using a 10–20 mg/g of Cu (II) and Pb (II) solution at a constant equilibrium state for 480 min.

Table 4: Isothermal constants of microextraction for various ACF samples

Target	Sample	Langmuir isotherm			Freundlich isotherm		
		$q_{\max}$	$K_L$	$R^2$	$K_F$	$n$	$R^2$
Cu (II)	ACF850	69.44	0.24	0.9936	9.61	0.38	0.9835
	ACF875	84.75	0.13	0.9953	4.25	0.46	0.9864
	ACF900	81.97	0.16	0.9916	5.94	0.44	0.9914
Pb (II)	ACF850	74.07	0.13	0.9885	3.24	0.56	0.9868
	ACF875	102.04	0.07	0.9919	3.42	0.43	0.9900
	ACF900	88.50	0.10	0.9908	3.43	0.50	0.9888

The  $\Delta S^\circ$  of the ACF samples is constant under certain conditions, therefore the value of  $\Delta S^\circ$  can be used as an alternative indicator of the microextraction trend between carbonaceous materials and metal species. As can be seen in Figure 3, it becomes apparent that  $S_{\text{BET}}$ -dependent landscapes of  $\Delta S^\circ$  as well as the dosage dependent on the aforementioned parameters were in a config-

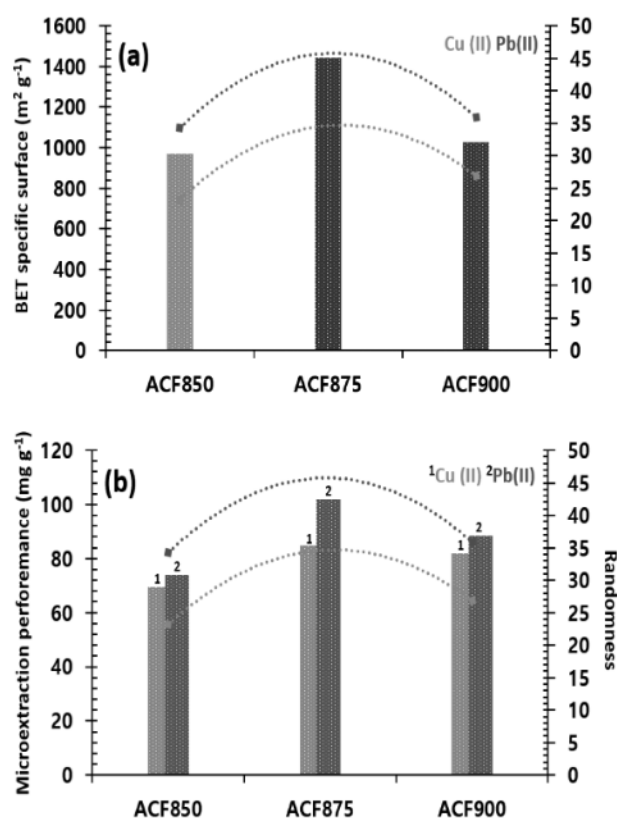


Figure 3: Correlation between randomness and affinity of metal species with a carbonaceous surface. Here, the x-axis refers to each ACF sample and the y-axis refers to: a) BET specific surface, b) microextraction performance showing the affinity trend via randomness

rational ensemble. In a strict sense, for the general affinity of metals with the adsorbent materials, the present data may be insufficient for determining the entire possibilities of landscapes. For instance, a change in materials and metals may cause another theoretical uncertainty. Nevertheless, thermodynamic and isothermal constants successfully underpinned the physiochemical characteristics studied above. Given that, probing such interacting systems could potentially shed some light on the field of microextraction and create interest in subsidiary studies by controlling the randomly distributed metal species at the surface of an adsorbent.

## 4 CONCLUSIONS

In conclusion, we examined the relationship between the randomness and affinity of metal species via a carbonaceous surface. By calculating thermodynamic and isothermal constants, we were able to determine the following findings:

1) There was a linear relationship between  $\Delta S^\circ$  and microextraction performance.

2) The  $S_{\text{BET}}$ , the temperature and the initial dosage of metals were considered altogether as an important environment for the maximum  $q_{\text{max}}$  value. Here, the Langmuir isotherm best described the experimental data.

3) Combining all the presented strategies, these findings offer a fundamental route for justifying  $\Delta S^\circ$  as an alternative indicator of the microextraction performance. Yet, a more persuasive approach and additional experiments are needed to eliminate the marginal error of material and metal samplings.

We expect these results to lay the path for predicting the affinity of metal species and thus designing highly efficient absorbent materials.

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