



# Comparison of Metal Adsorption from Aqueous Solutions on Coal and Char Remaining After In-situ Underground Coal Gasification (UCG)

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## Abstract

The aim of the study was to describe the sorption interactions between potentially toxic metals (Cd, Co, Cu, Pb) and materials from an underground coal gasification (UCG) experimental zone. These interactions seem to be significant in terms of the impact of in situ UCG on the groundwater environment. Sorption parameters were determined for two different sample types: subbituminous coal mined from the coal-bed and then subjected to gasification and coal char from the cavity formed by the UCG process. Laboratory-scale tests were carried out using deionized water and aqueous solutions of metals with increasing concentrations. The Freundlich isotherm model was applied to describe sorption phenomena due to nonlinear mass distribution of adsorbed metal ions as a function of equilibrium concentration and assuming physical interactions only. In addition, the efficiency of the tested sorbents for metal removal was calculated. In the case of subbituminous coal, the percent removal ranged from a minimum of 3.6–9.8% (for cobalt) to a maximum of 43.4–79.8% (for lead). Char removed metals more efficiently (min. 26.6–94.8% for cadmium; max. 98.5–99.9% for lead). Furthermore, the sorbates can be ranked according to the metal ion binding efficiency to sorbents in the following order: Co < Cd < Cu < Pb. The sorption characteristics of materials obtained from the post-UCG cavity may be used to evaluate the retardation parameters of inorganic pollutant migration in the environment around a georeactor.

**Keywords** Char residue · Cobalt · Cadmium · Copper · Lead · Freundlich isotherm

## Introduction

The underground coal gasification (UCG) technology obtains energy in the form of gas generated through the in situ gasification of coal deposits, which is then extracted to the surface. Gasification of the coal seam is initiated by

the ignition of part of the deposit, which is then sustained by the continuous supply of a gasifier (e.g. steam, oxygen, air). Gas produced via UCG can be used as a syngas or may be an indirect source of electricity.

Coal mines can use UCG to exploit those deposits that are not profitable for operation with conventional mining methods due to their unfavourable (e.g. deep) location or geological nature. However, despite its many economic and environmental advantages, the gasification of coal, like any oxidation process, generates a number of solid, liquid, and gaseous by-products that may contain substances hazardous to the water and soil environment (Bhutto et al. 2013; Campbell et al. 1979; Dalton and Campbell 1978; Humenick and Mattox 1978; Liu et al. 2007; Nakaten et al. 2014a, b; Sury et al. 2004). For this reason, it is extremely important to accurately monitor potential contaminants, both during and after the gasification process. In addition to basic organic pollutants such as phenols, benzene derivatives (BTEX), and polycyclic aromatic hydrocarbons (PAHs), the UCG process also generates a significant number of inorganic impurities,

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including changes in metal forms (Edgar et al. 1981; Liu et al. 2006a, b; Stuermer et al. 1982).

The presence of metals in the environment, such as Cd, Co, Cu, and Pb, is extremely significant in terms of their toxic properties, their high solubility, mobility, and ability for bioaccumulation. These metals are not biodegradable; therefore, they remain in the environment (Mishra et al. 2008; Vhahangwele and Mugeru 2015), and their bioaccumulation in the food chain can be harmful to humans, animals, and plants, even at relatively low concentrations (Chen et al. 2015; Jayakumar et al. 2015; Regmi et al. 2012). Especially relevant for the environmental impacts of coal are Se and As due to their substantial changes during combustion, making them more soluble. Detailed description of the behavior of As, Se, and other elements considered important during combustion and gasification of subbituminous coal and lignite, as well as how these elements leach from char and ash after UCG, is given by Strugała-Wilczek and Stańczyk (2015, 2016).

Recognizing the interaction of metals with materials near the in situ reactor is an integral element when comprehensively assessing the impacts of a UCG process on the groundwater environment. In particular, the phenomenon of sorption accompanying these interactions is considered one of the most effective, universal, and low-cost methods for blocking contaminant mobility (metal removal). The phenomenon of adsorption on solids is well-known, widely used on an industrial scale, and is suitable for metallic contaminants over a wide range of concentrations (Kamari et al. 2014; Park et al. 2016). Adsorption properties are determined by the degree of surface development, spatial structure, and the chemical nature of the adsorbent. Adsorbents can be both natural substances (zeolites, pumices) and chemically synthesised substances (active carbon, carbon blacks, silica gels, etc.). The presence of organic compounds forming complexes with metals in the sorbent may increase the effectiveness of their removal (Lach et al. 2006). While the carbon in the deposit has relatively few oxygen groups that are involved in sorption (e.g. of metals), carbon oxidation by gaseous or oxidizing liquids may increase the number of these groups, thereby increasing the sorption capacity of the solid material.

Due to its macroscopic properties, the adsorption phenomena can be distinguished into physical and chemical adsorption (chemisorption). Physical adsorption is determined by non-specific interactions (Van der Waals type, i.e., dispersive forces or dipolar interactions) and occurs on the surface of all solids (Atkins 2001). The adsorptive equilibrium state is described by sorption isotherms, which are curves that illustrate how the amount of an adsorbed substance varies depending on the concentration of the solution at a given temperature (Bielański 1998; Pigoń and Ruziewicz 1980).

As a part of this work, the sorption characteristics of materials obtained from an UCG cavity were investigated, mainly with regard to protecting the water and soil environment around the in situ reactor. Two types of sorbents were selected for the study—coal from the UCG experimental test area located in the “Barbara” experimental mine and the char from the cavity after completion of the process. Laboratory tests were conducted based on a static method, in a closed system, using increasing concentrations of metal ion solutions (Cd, Co, Cu, Pb). These metals were selected based on the results of the research on the leaching behaviour of metals from post-underground coal gasification cavity residues (Strugała-Wilczek and Stańczyk 2015, 2016). Sorption parameters based on the Freundlich isotherm model were determined for the sorption systems under test, assuming physical sorption. The efficiency of metal removal by both of the proposed sorbents was also estimated.

## Materials and Methods

### Sample Preparation and Analysis

The tests were carried out using representative samples of solid materials collected from the underground georeactor situated in the experimental mine ‘Barbara’ in southern Poland, within the administrative area of Mikołów city. The footprint plan of the mining area, places where char samples were collected, and groundwater sampling points surrounding the UCG reactor has been described elsewhere (Kapusta et al. 2013; Ludwik-Pardała and Stańczyk 2015).

There are two underground water reservoirs in the exploitation area, but there was no significant risk of reservoir contamination in the exploitation area. The georeactor was equipped with a collection and storage system and effluent was sent to the coke works’ water treatment plant. Groundwater quality, including changes of selected parameters (i.e. phenol and benzene) around the gasification site before, during, and after UCG in situ experiment was investigated by Kapusta et al. (2013).

The coal sample was taken from level 310, in the north-eastern part of the mining area, at a depth of 30 m. The average thickness of the seam was 1.5–2 m. As a result of the in situ UCG experiment, 22,114 kg of coal was gasified, and 71,764 Nm<sup>3</sup> (Nm<sup>3</sup>—normal cubic meter at 273 K and 1 bar pressure) of gas with an average calorific value of 3.75 MJ/Nm<sup>3</sup> was produced. The mass of coal gasified was determined by mass balance calculation of all of the elements in the coal and gasification reactants (air or oxygen) and the amount of all products (gas and liquids) obtained in the process. The produced gas came from both the coal’s volatile matter and coal matrix and it is not possible to distinguish the parts because in UCG different processes (like:

drying, pyrolysis, gasification, and combustion) are proceeding in parallel and overlapping. Using the same reactants for gasification, we may expect the same transformation of coal; however, at the beginning and end of the reaction, the degree of coal transformation would be different.

The char sample was extracted from the cavity that had formed as a result of gasification of a part of the coal deposit after 40 days of cooling and quenching the georeactor. The georeactor was cooled by liquid nitrogen, evaporated and sent to the cavity, with no water added, so as not to produce contact water samples. Details of the conducted UCG experiment are given in Table 1.

Approximately 4 kg of each of the coal and char samples from the UCG georeactor area were collected and standardized by fragmentation in a laboratory crusher and then left to air dry for 7 days until a constant mass was obtained (difference in mass during subsequent weighing did not exceed 5% within 24 h). More details about sample collection is provided by Ludwik-Pardała and Stańczyk (2015). The dried samples were sieved through a 10 mm

plastic sieve, yielding a target research material with a fraction of less than 10 mm. The samples were stored in sealed plastic containers until the tests were carried out. The sorbent samples underwent proximate and ultimate analysis, also the metal content was examined; the results are presented in Table 2.

The initial coal was a subbituminous coal with a high content of volatile matter and average calorific value. On the basis of the solid materials analysis (Table 2), it can be seen that the coal was intensively transformed during the gasification process into a substance with properties similar to coke, as evidenced by the very low volatile matter and high carbon content.

Porosity and surface area tests were carried out for the analysed geosorbents to characterize the physical properties of the carbonaceous materials. The tests were conducted using the Autosorb iQ gas sorption analyser (Quantachrome Instruments, USA). For comparison, sorption studies were also performed using NORIT®SX2 activated carbon (POCH, Poland). The BET surface areas of the

**Table 1** Conditions of the in situ UCG experiment (Kapusta et al. 2013; Wiatowski et al. 2012)

Origin/type of coal (seam)	Type of experiment/installation	Configuration of gasification channel	Length/diameter of gasification channel [m]	Gasification agent	Duration of the experiment [h]
Experimental mine 'Barbara'/subbituminous coal, type 31.2	In situ/non-pressure	Straight	15/0.15	Oxygen/Oxygen-enriched air	355

**Table 2** Proximate and ultimate analyses of sorbents and metal content in sorbents

Parameter	Unit	Origin and type of sorbent	
		Subbituminous coal from the experimental mine 'Barbara' (type 31.2)	Char residue from in situ UCG
Analytical state			
Moisture W	%	6.4	0.54
Ash A	%	16.5	7.92
Volatile matter content V	%	29.8	0.62
Heat of combustion Q <sub>s</sub>	kJ/kg	24,258	30,949
Calorific value Q <sub>i</sub>	kJ/kg	23,192	30,914
Total sulphur S	%	0.50	0.87
Hydrogen content H <sub>t</sub>	%	3.7	0.10
Carbon content C <sub>t</sub>	%	58.0	89.4
Nitrogen content N	%	0.9	0.69
Oxygen content O*	%	14.0	0.48
Cobalt Co	mg/kg	18	10
Cadmium Cd	mg/kg	< 1	< 1
Copper Co	mg/kg	27	15
Lead Pb	mg/kg	13	9.0

\*Oxygen calculated as: (O) = 100 - (W) - (A) - (C<sub>t</sub>) - (H<sub>t</sub>) - (S) - (N) (%)

sorbents were examined to help assess how surface area might have affected metal removal.

Based on the results (Table 3), it can be concluded that high temperatures during coal gasification caused porous structures to develop. The effect of UCG ‘activation’ can be noticed in the increasing BET surface area of the coal char, six times that of the raw subbituminous coal, and the BET surface area of activated carbon was more than two orders of magnitude greater than the other two sorbents. The total pore volume of UCG char increased almost four times, with a nearly twofold decrease in the average pore diameter compared to raw coal. Thus, the UCG char was ‘activated’ during gasification. The total pore volume of the activated carbon was more than 100 times greater (with a nearly fourfold smaller average pore size) than that of the raw coal.

### Static Sorption Tests

The sorption parameters of the subbituminous coal and the post-processed char remaining in the cavity after the in situ UCG process were determined using laboratory-scale tests based on the static method (in a closed system). Based on previous research on the leaching behaviour of metals from post-underground coal gasification cavity residues (Strugała-Wilczek and Stańczyk 2015, 2016), sorption tests were conducted on four metals (cobalt, cadmium, copper and lead). The selected metals tend to be leached by water from post-UCG residues, which, due to their toxic properties, are a potential threat to the water and soil environment in the georeactor vicinity. Standard stock solutions of metals with certified analyte concentrations (supplemental Table S-1) were used to prepare the sorbate solutions.

Six aqueous solutions of the selected metals with increasing analyte concentrations were prepared (Table 4). The concentration ranges and the mutual ratios of metal concentrations were selected based on the analysis of the physicochemical composition of groundwater occurring in the area of the in situ gasification and on the basis of the metal content in the eluates obtained from water leaching post-UCG residues (Strugała-Wilczek and Stańczyk 2015, 2016). For each prepared sorbate solution, the pH was determined potentiometrically using a PHM 240 pH meter from Radiometer (Denmark), and metal concentrations were determined by plasma emission spectrometry (ICP-OES) using an Optima 5300 DV analyser from Perkin Elmer (USA). The limits of quantification for metals were: for Cd 0.0002 mg/dm<sup>3</sup>, for Co 0.0010 mg/dm<sup>3</sup>, for Cu 0.0020 mg/dm<sup>3</sup>, and for Pb 0.0050 mg/dm<sup>3</sup>.

A 20 g sample of the corresponding sorbent (subbituminous coal, char residue, and activated carbon) was placed in a plastic container and then covered with 200 cm<sup>3</sup> of aqueous solutions of the selected metals with decreasing concentrations (I–VI) and deionized water (to determine possible desorption). The mixtures were shaken in a GFL3040 laboratory rotating shaker (Germany) in tightly sealed and Teflon-protected containers. The static test method was consistent with the European Standard EN 12457-2 (2002) elution test method. The full cycle included 2 h of shaking, 4 h of standing, 1 h of shaking, 16 h of standing, and a final 1 h of shaking. The mixtures were shaken at 15 revolutions per min. They were then left in a static state until the sorption equilibrium had been reached and the suspended matter had settled. The obtained extracts were filtered under reduced pressure, minimizing the contact with air, and using

**Table 3** Selected physical properties of the tested sorbents

Parameter	Subbituminous coal from the experimental mine ‘Barbara’	Char residue from in situ UCG	Activated carbon NORIT®SX2
BET surface area [m <sup>2</sup> /g]	2.46	14.8	888
Total pore volume [cm <sup>3</sup> /g]	0.007	0.027	0.76
Average pore size (diameter) [nm]	12.1	7.19	3.40

**Table 4** Composition of aqueous solutions of the selected metals

Initial solution	pH ± U	c <sub>0</sub> ± U [mg/dm <sup>3</sup> ]			
		Co	Cd	Cu	Pb
I	6.07 ± 0.20	5.28 ± 0.53	1.00 ± 0.10	4.89 ± 0.49	10.0 ± 1.0
II	6.11 ± 0.20	2.14 ± 0.21	0.409 ± 0.041	1.99 ± 0.20	3.86 ± 0.39
III	6.18 ± 0.20	1.07 ± 0.11	0.204 ± 0.041	0.97 ± 0.19	1.91 ± 0.19
IV	6.28 ± 0.20	0.526 ± 0.053	0.100 ± 0.020	0.477 ± 0.095	1.00 ± 0.10
V	6.30 ± 0.20	0.263 ± 0.053	0.051 ± 0.010	0.226 ± 0.045	0.497 ± 0.099
VI	6.22 ± 0.20	0.053 ± 0.013	0.0105 ± 0.0026	0.046 ± 0.012	0.110 ± 0.027

c<sub>0</sub> analyte concentration in the sorbate solution, U expanded uncertainty for coverage factor k = 2

membrane filters with a pore diameter of 0.45 μm (Millipore Merck, Germany). The shaking and determination of sorption equilibria were carried out at a constant temperature of 298 K. For all obtained filtrates, the pH was measured and metal concentrations were determined as discussed above (Tables 5 and 6).

## Results and Discussion

### Analysis of the Sorbate Solution Compositions After the Sorption Tests

An analysis of the metal equilibrium concentrations in the solutions after sorption tests ( $c_i$ ) allowed adsorption isotherm parameters to be determined and the sorption interactions between the metals and materials obtained from the georeactor environment and between the metals and activated carbon to be examined. The concentrations of the tested metals in solution were less after the sorption tests than in the initial solutions (Table 4), demonstrating proof of sorption. All solutions had a stable pH of ≈ 6.3. The filtrate physicochemical analysis results obtained after the static sorption tests with subbituminous coal and char are given in Tables 5 and 6. Due to the total sorption that occurred in

the analysed range of concentrations of the studied metals using activated carbon, it was not possible to describe this system using adsorption isotherms.

### Effectiveness of the Tested Geomaterials in Metal Removal

The percentage efficiency of metal removal by sorbents for the tested systems was estimated using the following formula (Ahmed and Theydan 2012; Kamari et al. 2014; Tan et al. 2015):

$$Removal\ efficiency\ [\%] = \frac{(c_0 - c_i)}{c_0} \times 100\% \quad (1)$$

where:  $c_0$  = concentration of analyte in the stock solution [mg/dm<sup>3</sup>] and  $c_i$  = equilibrium concentration of the sorbed component in sorbate solution [mg/dm<sup>3</sup>].

For all tested metals, the UCG char showed better sorption capacity than the subbituminous coal (Fig. 1a–d). For coal, removal efficiency value varied from 3.6 to 9.8% for cobalt (Fig. 1a) to 43.4–79.8% for lead (Fig. 1d). The UCG post-process char was much more efficient in removing contaminants. As was seen in the case of coal, cobalt ions were the least sorbed from solution (from 26.6 to 94.8%) (Fig. 1a),

**Table 5** Composition of sorbate solutions after sorption tests with hard coal

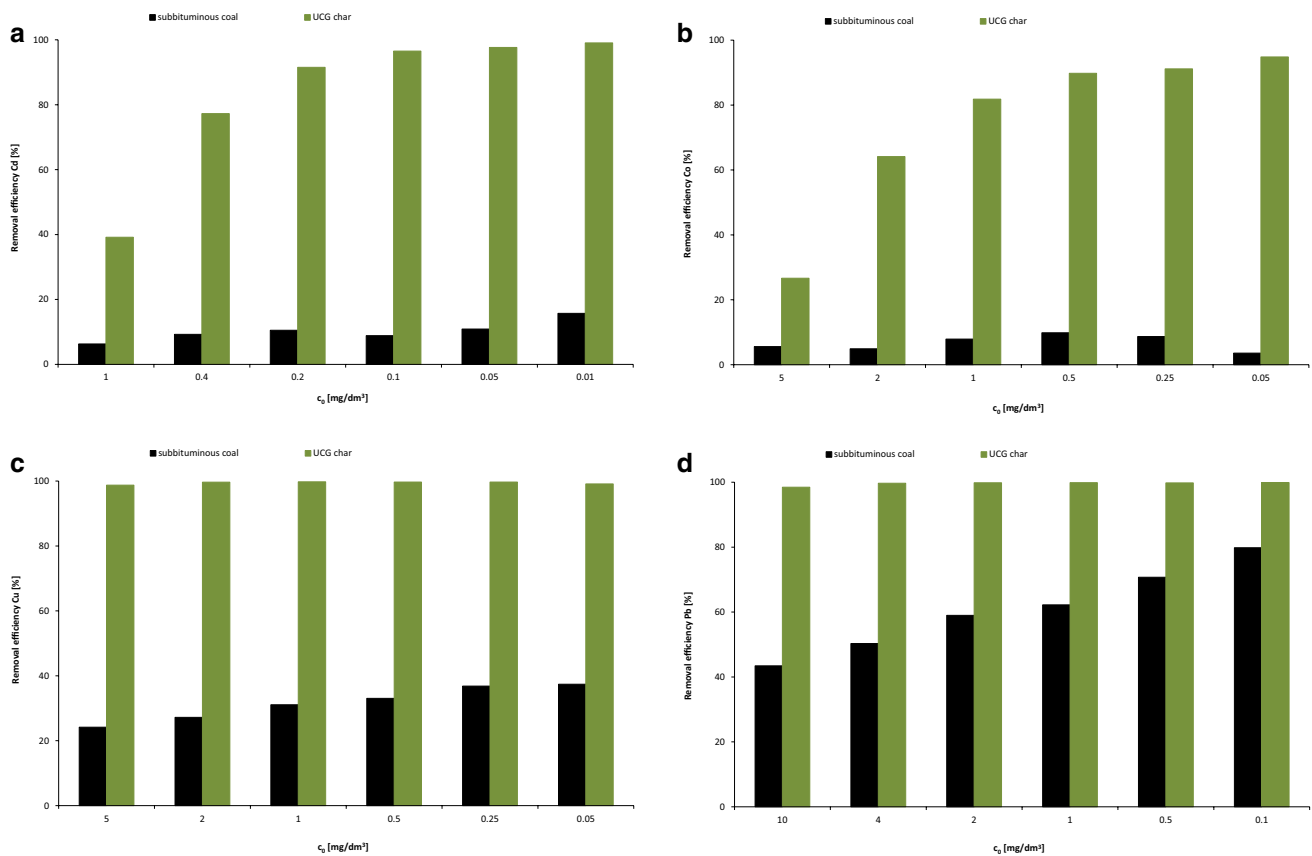
Solution after sorption on subbituminous coal	pH ± U	$c_i \pm U$ [mg/dm <sup>3</sup> ]			
		Co	Cd	Cu	Pb
H <sub>2</sub> O deionized	6.26 ± 0.20	0.106 ± 0.021	0.0009 ± 0.0002	0.060 ± 0.015	0.0225 ± 0.0056
I	6.25 ± 0.20	5.09 ± 0.51	0.940 ± 0.094	3.77 ± 0.37	5.69 ± 0.57
II	6.26 ± 0.20	2.14 ± 0.21	0.372 ± 0.037	1.51 ± 0.15	1.94 ± 0.19
III	6.26 ± 0.20	1.09 ± 0.11	0.184 ± 0.036	0.73 ± 0.15	0.80 ± 0.16
IV	6.26 ± 0.20	0.581 ± 0.058	0.092 ± 0.018	0.380 ± 0.076	0.403 ± 0.081
V	6.26 ± 0.20	0.346 ± 0.069	0.046 ± 0.012	0.203 ± 0.041	0.168 ± 0.042
VI	6.26 ± 0.20	0.157 ± 0.031	0.0098 ± 0.0024	0.089 ± 0.022	0.044 ± 0.011

$c_i$  analyte equilibrium concentration in sorbate solution after sorption,  $U$  expanded uncertainty for coverage factor  $k=2$

**Table 6** Composition of sorbate solutions after sorption tests with UCG char

Solution after sorption on UCG char	pH ± U	$c_i \pm U$ [mg/dm <sup>3</sup> ]			
		Co	Cd	Cu	Pb
H <sub>2</sub> O deionized	6.26 ± 0.20	0.0008 ± 0.0002	n.d.	0.0008 ± 0.0002	n.d.
I	6.21 ± 0.20	3.878 ± 0.038	0.6100 ± 0.061	0.0608 ± 0.0152	0.1522 ± 0.038
II	6.21 ± 0.20	0.768 ± 0.077	0.0930 ± 0.018	0.0066 ± 0.0016	0.0120 ± 0.003
III	6.22 ± 0.20	0.194 ± 0.038	0.0174 ± 0.0043	0.0024 ± 0.0006	0.0030 ± 0.0007
IV	6.22 ± 0.20	0.053 ± 0.013	0.0035 ± 0.0008	0.0014 ± 0.0003	0.0014 ± 0.0003
V	6.27 ± 0.20	0.0233 ± 0.0058	0.0012 ± 0.0003	0.0006 ± 0.0002	0.0010 ± 0.0002
VI	6.26 ± 0.20	0.0028 ± 0.0007	0.00010 ± 0.00002	0.0004 ± 0.0001	n.d.

$c_i$  analyte equilibrium concentration in sorbate solution after sorption, *n.d.* not determined (below the method's limit of quantification),  $U$  expanded uncertainty for coverage factor  $k=2$



**Fig. 1** Cadmium (a), cobalt (b), copper (c) and lead (d) removal efficiency by the tested sorbents

and lead ions were adsorbed to the greatest extent (from 98.5 to 99.9%) (Fig. 1d). Very good sorption was also obtained for the char–copper system, where 98.8–99.7% of the metal ions were sorbed from the solution (Fig. 1c). For both copper and lead, the char removed almost 100% of the metals in the entire tested concentration range. The post-process char’s ability to adsorb cobalt and cadmium definitely decreased with increasing sorbate concentration (Fig. 1a, b). The relationship between the sorption capacity of carbon and sorbate concentration has an undisturbed monotonic character in the cases of copper and lead (Fig. 1c, d); for cadmium, a slight disturbance of the trend can be observed (Fig. 1a), while in the case of cobalt, the disturbance is worse, especially at low concentrations (Fig. 1b).

Based on the estimated percentage removal efficiency of the metals by the sorbents, it is possible to rank the tested sorbates in terms of the efficiency of metal ion binding ability in ascending order, from the least to the most reactive:  $\text{Co} < \text{Cd} < \text{Cu} < \text{Pb}$ . Importantly, if a metal mixture is used, the sorption effects may be significantly less than when analysing a single metal solution (Park et al. 2016). As Harter (1992) has shown, when comparing the competitive sorption of metals with the behaviour of single metals, competitive system adsorption usually occurs to a lesser extent.

Effective removal of contaminants can be achieved by applying active carbons with highly developed microstructures, the activation of which requires specialized activators such as  $\text{FeCl}_3$  or  $\text{KOH}$  (Kilic et al. 2011; Theydan and Ahmed 2012). The alternative use of solid post-UCG residues to effectively adsorb contaminants is convenient and beneficial regarding the process’ impact on the natural environment. Moreover, the potential self-cleaning of the UCG cavity after the exploitation phase has no additional costs and is an integral element of the UCG process.

### Adsorption Isotherms

The sorption interactions between the tested metals and materials obtained from the in situ UCG georeactor environment were described by adsorption isotherm parameters. Due to the nonlinear mass distribution of the adsorbed metal ions as a function of equilibrium concentration, and assuming only physical interactions, the sorption parameters were determined for the nonlinear sorption model described by the empirical Freundlich equation:

$$c_a = K_F \times c_i^n \quad (2)$$

where:  $c_a$  = amount of substance adsorbed per unit mass of adsorbent [mg/g],  $c_i$  = equilibrium concentration in sorbate solution [mg/dm<sup>3</sup>],  $K_F$ ,  $n$  = constants characteristic for a given system and a given temperature. The parameter  $K_F$  additionally depends on the size and condition of the adsorbent surface.

The amount of substance adsorbed per unit mass of sorbent was calculated from the formula:

$$c_a = \frac{(c_0 - c_i + c_d) \times V}{W} \tag{3}$$

where:  $c_0$  = concentration of analyte in the stock solution [mg/dm<sup>3</sup>],  $c_d$  = concentration of desorbed analyte [mg/dm<sup>3</sup>],  $V$  = volume of the solution [dm<sup>3</sup>], and  $W$  = sorbent mass [g].

The desorption concentration is the equilibrium concentration  $c_i$  determined by a static test in the sorbent-deionized water system. For the char, the desorption concentration was negligible (Table 6) and its value was assumed to be zero. Isotherm parameters were estimated by unweighted least squares linear regression. Freundlich sorption isotherm coefficients for all analysed sorption systems are provided in supplemental Table S-2. The adsorption isotherms are presented in Fig. 2a–d.

In the Freundlich equation, the  $K_F$  factor is a constant referring to sorption capacity, while  $n$  is a parameter related to the sorption intensity, which changes together with the heterogeneity of the material. A value of  $1/n$  between 0 and 1 typically indicates good sorption ability (Freundlich 1906).

For cobalt sorption on carbon, the exponent  $n > 1$ , may indicate that the amount of adsorbed substance increases more slowly than its concentration in solution after reaching equilibrium (Bielański 1998). For each isotherm describing the char–metal system, there is a characteristic deviating point that corresponds to the highest equilibrium concentration of the metal. This point is particularly visible in the case of Cd and Co (Fig. 2a, b, respectively). This can be explained by saturation of the adsorbent surface and by the interactions between solvates that increase in proportion to the increased concentration of metal ions in solution.

### Impact of the UCG Process on the Change of Sorption Properties of the Examined Geomaterials

The sorption properties of the studied geosorbents were evaluated based on the  $K_F$  and  $n$  parameters from the Freundlich isotherms that characterize a given system at a

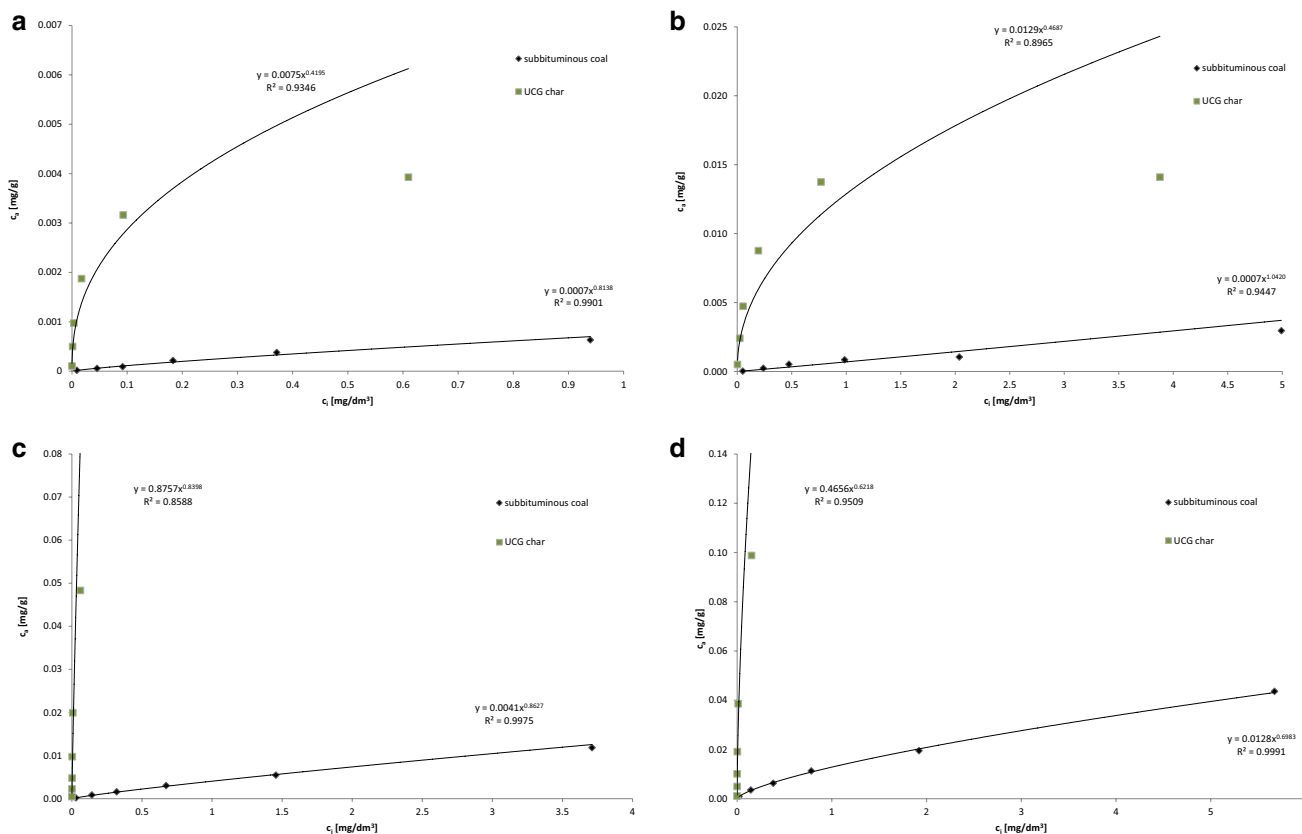
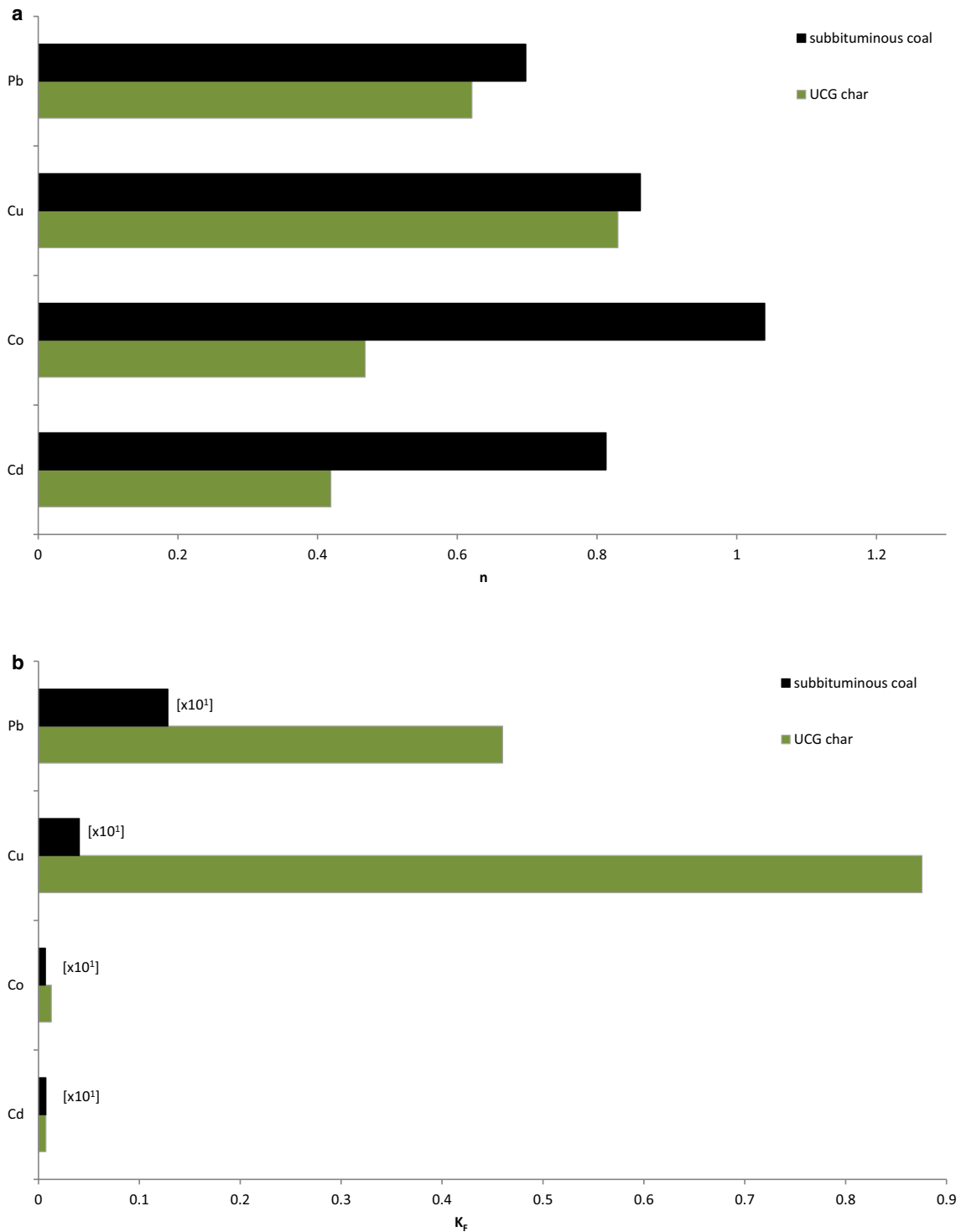


Fig. 2 Freundlich isotherms for: a cadmium, b cobalt, c copper and d lead with the tested sorbents

given temperature. The sorption abilities in the group of studied geomaterials and tested inorganic parameters were compared based on a summary of the  $K_F$  and  $n$  constants from the Freundlich isotherm equations for the individual sorption systems (Fig. 3a, b).

According to Toul et al. (2003), the type of isotherm determined by  $K_F$  and  $n$  determines the sorption mechanism of the analysed chemical compound with the specified geomaterial. Knowledge of the  $K_F$  parameter, whose value depends on the size and state of the adsorbent surface,



**Fig. 3** Values of the: **a**  $n$  parameter and **b**  $K_F$  parameter of Freundlich isotherms for the tested systems



allows one to compare the sorption capacities of tested sorbents; the greater their sorption capacity, the higher their  $K_F$  value. The constant  $n$  in the Freundlich isotherm equation is a directional coefficient equal to the tangent of the slope angle in the logarithmic coordinate system. Accordingly, the intensity of the sorption phenomena is directly proportional to the value of  $n$  (Ignatowicz 2011). A low  $n$  value in the isotherm equation is characteristic for a system in which sorption occurs more intensively in the low sorbate concentration range; in this case, the sorption intensity decreases as the sorbate concentration increases. When  $n$  is in the range from 0 to 1, the higher the  $n$  value, the less intense the decrease in sorption with the concentration of the sorbed compound. If  $n$  exceeds one, the sorption intensity is high; in such systems, sorption intensity increases exponentially with sorbate concentration.

Figure 3a, b shows that the UCG char from the region of the gasification experiment in the ‘Barbara’ experimental mine has a greater sorption capacity than raw subbituminous coal relative to the tested contaminants. The change in sorption capacity of the post-process char was compared to raw coal (Table 7).

The data presented in Table 7 show that the UCG process produces a char whose sorption capacity significantly exceeds the sorption capacity of raw coal, from 10 times in the case of cadmium to almost 200 times for copper. This large increase is due to a number of physicochemical changes in the carbon matter that occurred in the direct vicinity of the UCG georeactor, which may be analogous to those that occur during the synthesis of carbon adsorbents (activated carbons). A typical biochar is less carbonized than activated carbon because more hydrogen and oxygen atoms remain in its structure (Hale et al. 2012; Mohan et al. 2012, 2014). This carbonization occurs at high temperatures, forming the so-called elementary crystallites of graphite. Their arrangement is irregular due to the presence of free spaces filled with amorphous carbon and tars, and so has poorly developed adsorption properties. Sorption capacity increases during chemical activation (by heating the char at high temperatures with the addition of appropriate chemical compounds) or physical activation (Choma and Kloske 1999), such as occurs in the UCG process, when the oxidizing agents present, such as steam, carbon dioxide, oxygen, or a mixture of these gases, partially gasify the carbon. Oxygen is the most active oxidizing agent and carbon dioxide is

the least active (Marsh et al. 1997). In the UCG experiment from which the sorbent materials were obtained, oxygen and oxygen-enriched air were used as oxidizing agents, and the char that formed may have had characteristics similar to those of activated carbon (total surface, pore volume). Park et al. (2016) claimed that carbonized carbon from a UCG cavity may be a low-cost alternative to activated carbon for the sorption of organic and inorganic contaminants (including metals).

The properties of the porous structure of post-process char, such as pore shape and volume, specific surface area, and the pores’ mutual arrangement, not only define the physical properties of the material (density and strength) but are also responsible for the thermal conductivity and mass flow that are relevant in the thermochemical treatment processes (Howaniec 2016; Rouquerol et al. 1994). The high temperature that occurs during pyrolysis can be generally assumed to positively affect the development of the char’s porous structure and is reflected in the increased specific surface area and total pore volume (Tremel et al. 2012; Yangsheng et al. 2010; Yu et al. 2007). The development of this porous structure can be attributed to the intense release of moisture and volatile substances at high temperatures in the initial phase of pyrolysis during coal swelling. The porosity of the coal pyrolysis product also strongly depends on the properties of the initial fuel.

### Conclusions

We compared the sorption characteristics of subbituminous coal and solid materials from the UCG process. Static sorption tests were carried out using solutions containing increasing concentrations of metal ions (Cd, Co, Cu and Pb). Sorption parameters were determined using Freundlich isotherms, which worked better when sorption was conducted using subbituminous coal ( $R^2$  of 0.9447 for Co to 0.9991 for Pb) and not quite as well for UCG char ( $R^2$  from 0.8588 for Cu to 0.9509 for Pb). The post-UCG char was found to have a better sorption capacity than the raw subbituminous coal due to the char’s increased surface, as well as the thermal transformation caused by the gasification process and coal oxidation at high temperatures (temperature during the experimental UCG were estimated between 800 and 1200 °C).

The sorbent efficiency in metal removal depended on the metal concentration in solution, and for coal varied from 3.6 to 9.8% for cobalt and 43.4–79.8% for lead. The UCG post-process char was much more efficient, and the metal removal efficiency varied from 26.6 to 94.8% for cobalt to 98.5–99.9% for lead. Based on the metal removal efficiency, the sorbates were ranked in terms of metal ion binding efficiency in the following order: Co < Cd < Cu < Pb.

**Table 7** Relative change in the sorption capacity of coal after the UCG carbonization process (in situ experiment, experimental mine ‘Barbara’)

Parameter (sorbate)	Cadmium	Cobalt	Copper	Lead
Relative change in the sorption capacity [%]	914	1755	19653	3485

Determining the sorption parameters for the tested solid materials makes it possible to construct a model for the dispersion of inorganic contaminants in the groundwater and soil environment in the vicinity of in situ UCG reactors.

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