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Lignite as a natural active immobilization system for surface/drainage water polluted by fertilizers

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The quality of surface and drainage water is key for the health of nature; therefore, their contamination levels should be maintained under safe limits. This study focuses on water sampled from the Říčka tSream in the Czech Republic, which is contaminated mainly by nitrates and phosphates originating from fertilizers. Additionally, the content of heavy metals was monitored. The measured concentrations of Cd and Zn were below the limit of detection, while Cu and Pb remained below safe limits except during summer, likely due to the dry season. Concentrations of nitrates and phosphates exceeded the limiting values in all cases. Batch adsorption experiments using lignite were performed with both model solutions to determine adsorption capacity, which decreased in the order Pb > Cu > nitrates > phosphates. The experiments with real water samples from the Říčka Stream showed that lignite can effectively immobilize the studied pollutants. The adsorption efficiency was higher than 70% in all cases. The majority of the adsorbed pollutants remained in the immobilized forms both in the experiments with the model solutions and real water samples. An increased leachability was observed for nitrates; however, the equilibrium concentrations of nitrates after adsorption as well as their leachable form were under safe limits. Lignite can be considered an effective and low-cost adsorbent for the removal of pollutants from real water.

Environmental significance

The main novelty of our study lies in the investigation of a locality with international significance that has never been studied scientifically, despite its proximity to the Cairn of Peace Memorial (the Battle of Austerlitz), and the combination of analysing real water samples with adsorption experiments to investigate adsorption ability of lignite, and the application of lignite as a natural eco-friendly material to treat sampled real water. The contaminations of water in this locality arose mainly from agricultural fertilizers and industrial activities; therefore, nitrates, phosphates and heavy metals were monitored as main pollutants due to their harmful effects on the environment and human health. The leachability was tested to suppress their mobility and bioavailability. Our study showed that monitoring endangered localities and applying lignite for pollutant immobilization can be used as a sustainable approach to keep the contamination of natural and drainage water within safe limits.

1 Introduction

Modern society generates an increasing input of different contaminants which have harmful effects on the environment and people's health. Our life is based on water, which is necessary for the existence of all living organisms. Thus, the quality of the water is essential for the health of all living things. The contamination of water by hazardous pollutants, such as fertilizers, heavy metals, pharmaceuticals, dyes, and pesticides, is a serious worldwide problem.[1–7] Thus, one of the fundamental problems in society is the development and implementation of efficient and ecological technologies for the removal of pollutants from the environment to reduce risk factors for ecosystems and the health of people.[2,8–14] The water regime in nature is affected by climatic conditions and can be very dynamic as a result of changes in weather. Changes in temperature and precipitation can result in fluctuations in the concentrations of pollutants in waters. An increase in temperature can result in a decrease in river flows, which means that a potential input of pollutants cannot be sufficiently diluted, and their concentrations can increase above safe limits. In contrast, stormwater can be connected with increased runoff, which can dilute surface and drainage water, but it can lead to flooding in urban areas and a decreased water quality.[4,15–17] The quality of surface and drainage water can fluctuate depending on climatic conditions (precipitation and temperature). If it is exposed to relatively frequent or permanent sources of pollutants, its contamination can exceed safe limits over time.

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Our study focuses on two groups of pollutants: fertilizers and metal ions. Increasing fertilizer use has resulted in the leakage of pollutants from agricultural lands to aquifers. Given the recent nature of this increase, groundwater pollutant concentrations, loads, and exports may likewise be on the rise, as contaminants infiltrate deeper into the aquifers.[3,18,19] Nitrogen, phosphorus, and potassium fertilizers are used as basic fertilizers for agricultural production.[18] The application of these fertilizers can affect bacterial community, soil properties, and groundwater quality. Some authors regard the role of N fertilization as more significant than that of P and K fertilization.[18,20–23] Wade *et al.*[24] stated that the loss of nitrates and phosphates from farms and farmland can be enhanced by climate change, which can potentially worsen freshwater eutrophication. Climate change can cause droughts connected with an increase in the concentration of pollutants in surface waters. On the basis of the above-described results published by other authors, we decided to focus on nitrates and phosphates in our study. Our investigation was complemented by the monitoring of metal ions that can cause distressing effects on the ecological balance of the aquatic environment, and pose a health hazard to aquatic organisms.

While nitrates and phosphates enter the environment from fertilizers, the major sources of heavy metals in nature are mainly from industry, mining, metal plating, corrosion, and electronic device manufacturers. Sediments can also be considered a source of pollutants, such as metals.[25] Some metals can affect the biological functions and growth of plants, while other metals can accumulate in one or more different organs causing various diseases.[26] The most monitored metals are As,[25,27] Cd,[25,27–30] Cr,[27–30] Cu,[27–33] Fe,[27,28,33] Hg,[25,27,30] Mn,[28,33] Ni,[25,27–30,33] Pb,[25,28–30,33–35] and Zn.[27,28,30,31,33,34] Chon *et al.*[25] focused on the role of sediments in the metal pollution of river catchments. Their results showed that the highest rate of release determined from these sediments was for Pb in comparison with Ni, Cd, and Hg (in this order). De Nicola *et al.*[33] monitored six different metals in two Italian regions (Campania and Tuscany). They reported that urban areas in both regions are the main sources of metal pollution, with metal concentrations in soils significantly higher than those in plants. Additionally, the concentration of different metals (Cu, Fe, Mn, Ni, Pb, and Zn) depended on the type of metal and location. Buragohain *et al.*[32] compared the competition of Cu in two different soils. They performed traditional adsorption experiments and predicted the fate of Cu by fitting data to the Freundlich and Langmuir isotherms. They found that the predicted contamination was higher for the Cu solution without other metals. Comparatively, the presence of other metals decreased Cu bioavailability, which was affected by the amounts and types of metals in used in the solutions. Van Ooort *et al.*[34] monitored Zn and Pb contents in 173 soil samples. They considered Pb a less-mobile metal in comparison with Zn. They also compared the time development of the Zn/Pb concentration ratio in their samples. They determined different Zn/Pb ratios for soils under different land use based on the implication that several decades after industrial activity, a fraction of metal remains in the samples, depending on the land use and soil conditions. Alvarez-Bobadilla *et al.*[28] modelled the fate and migration of nutrients and heavy metals in Lake Chapala in Western-Central Mexico and compared their modelled results with their experimental data. The best approximation for the measured values of the metals was obtained for Ni. It was confirmed from the simulations that the fate and migration of pollutants can provide a prediction of pollution scenarios. Detailed reviews on different hazardous pollutants in nature were published by Aryal *et al.*,[8] Gaur *et al.*,[27] Kumar *et al.*,[30] Rathi *et al.*,[6] and Shahid *et al.*[35]

It is necessary to solve this problem of pollution by striving to remove pollutants from natural systems, such as soil, natural water and wastewater and reducing their inputs in nature. Nowadays, low-cost sorbents avert this problem. Esfandiar *et al.*[29] studied the sorption of Cd, Cr, Cu, Ni, Pb, and Zn from stormwater runoff. They used commercially available sorbents, such as blast furnace slag, coconut coir fibres, waste tire crumb rubber and biochar. The removal efficiency was the highest if adsorption was performed with a single metal and was the lowest with multiple metals in the presence of different other contaminants (such as nutrients and polycyclic aromatic hydrocarbons). When humic acids were added in the studied systems, soluble metal–humic complexes were formed. In general, the waste tire crumb rubber and biochar had higher efficiencies in comparison with the other sorbents; Cr, Cu, and Pb were more adsorbed than Cd, Ni, and Zn. Smol and Włóka[7] used opoka rock as a natural sorbent for the removal of NO_3^-, NH_4^+, PO_4^{3-}, and organic carbon from real waters in batch and column experiments. The efficiency of the batch experiments was >80%, while a lower efficiency was observed for the column experiments (25–68%). Different possibilities for the removal of nutrients and metals from aqueous and soil systems were described in the reviews of Coccia and Bontempi,[2] and Rathi *et al.*[6] They stated that adsorption and ion exchange are still widely used methods for the removal of pollutants from natural systems, along with low-cost sorbents from agricultural waste, waste from the paper industry or natural materials, such as silica, fly ash, peat, sludge and lignite.[2,6,14,34,36,37] The traditional adsorption approach (in some cases) has been replaced by more advanced materials and methods, such as biochar, graphite oxides, carbon nanotubes, metal organic structures, magnetic and nano composites, reverse osmosis, coagulation, disinfection water treatment and anaerobic processes in biological-based technologies.[2,6,14,35,37]

Our study focuses on traditional batch adsorption where lignite is used as an environmentally friendly low-cost adsorbent. Lignite is rich in humic substances as well as inorganic (ash) material, which resulted in the high adsorption capacity and efficiency of this young coal.[38–48] Lignite has been mainly investigated as an adsorbent for metal ions;[38–51] however, it has been used to a lesser degree for nutrients.[39,50,51] Many authors (*e.g.*[38,40–43,45–48]) have realized that traditional batch experiments can be used to investigate the adsorption of metals on lignite. Some of these authors (*e.g.*[44,49]) compared the results of their batch and column experiments and found that the adsorption capacity was much lower for the lignite column. Desorption in the column experiments was much higher in comparison with the batch experiments. This result means that weaker bonds were probably formed as a result of a shorter contact time (metal–lignite). Published studies have largely focused on adsorption equilibrium and data fitting using the traditional Langmuir,[37,38,40,42,43,45,46] Freundlich[37,38,40,45,46] isotherms or the combined Langmuir-Freundlich model.[41] Additionally, some of these studies have dealt with adsorption kinetics.[38,40–43,45,46] The effects of experimental conditions, such as pH,[38,40–43,45] temperature,[37,40,46] and particle size[37,47] were also studied. If metal ions from mixtures containing different types of metals were adsorbed, then competition resulted in lower adsorption amounts when compared with adsorption for the individual metals. Additionally, the metals with a higher affinity for lignite (especially Cu and Pb) suppressed the adsorption of metal ions with a lower affinity for lignite.[40,45]

Regarding nutrients, mainly nitrogen (in the form of NH_4^+ and NO_3^-) and phosphorous (in the form of $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) have been monitored and their removal from natural systems was investigated.[39,50,53] Published studies have dealt with the effect of the application dose of lignite on N loss from broiler litter,[39] phosphate sorption in an acidic soil,[50] and the removal of different micropollutants and nutrients (phosphorus, nitrogen, and dissolved organic carbon) from household wastewater.[51]

As mentioned above, lignite was used in this study as a functional material for the removal of several types of pollutants from water. Our study was divided into three sections. The first section dealt with the monitoring of real water sampled from the side opening of a canal in the Říčka Stream, which is located in Kobylnice (near Brno) in the Czech Republic; specifically, the canal is located in an agricultural area. Therefore, increased water pollution can be expected due to the fertilization of the surrounding soil. Nine sampling points were chosen, and water samples from these points were analysed. The content of nitrates, phosphates (originating from fertilizers) and metal ions (the supplementary analysis of which was chosen on the basis of findings presented in the above-described studies) were determined. It was found that copper and lead were detected in our samples and the content of other metals was immeasurable; therefore, our study only focused on these two metals. The second section of our study dealt with lignite as an adsorbent for copper and lead ions, nitrates, and phosphates. Traditional batch adsorption experiments with lignite were performed in which the adsorption effectiveness and capacity of lignite for adsorbing pollutants were determined. In the last section of our study, lignite was applied to the water samples analysed in the first section of our study. In this section, we evaluated the effectiveness of lignite for the removal of pollutants from real waters. To investigate the stability of the formed complexes and bond strength of the pollutants adsorbed on lignite, the lignite samples with adsorbed pollutants were tested for their capacity to leach these adsorbed pollutants back into water (desorption). The overall objectives of our study were to investigate lignite as a material for removing pollutants from aqueous solutions and real waters and to evaluate the leaching of pollutants from lignite back into water. By achieving these objectives, we could deduce the potential for the utilization of lignite as a functional material for the removal of pollutants from water.

2 Experimental

2.1 Materials

Lignite was obtained from the Mikulčice locality in the southern region of Moravia near Hodonín (Czech Republic). A detailed characterization of the obtained lignite has been published in the literature.[40,41,52] The obtained lignite was used in its natural state, after the evaporation of its freely bound water, allowing for equilibration with the ambient laboratory atmosphere of about 25 °C. This step resulted in a final equilibrium moisture content of about 7 wt%. Lignite with a particle size fraction of less than 0.2 mm was used for the sorption studies.

Cadmium(II) chloride, copper(II) chloride, lead(II) chloride, zinc(II) chloride, potassium nitrate, and potassium phosphate were purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2 Sampling and analysis of real water

Water was sampled from the side opening of a canal in the Říčka Stream located in Kobylnice (49°8′17 N, 16°43′55 E) near Brno in the Czech Republic (see Fig. 1). Sampling was conducted on three different dates: June 6, 2023, August 28, 2023, and September 14, 2023. Sampling in July was not feasible due to the dry season and the absence of water at some sampling locations. Nine sampling locations were chosen, and these water samples were analysed. The concentrations of the metal ions were measured by in-electrode coulometric titration (Eca-Flow 150 GLP, Istran, Bratislava, Slovakia) based on the direct electrochemical conversion of the analyte species in the pores or a thin layer of the electrode. The metal ions were electrochemically deposited from the flowing sample solution onto the porous working electrode. The deposition was performed by applying a suitable potential. In the next step, the deposit was stripped galvanostatically. The stripping chronopotentiogram, where the peak areas were proportional to metal concentrations (calculated on the basis of the calibration lines), was then recorded. All metal ions (Cd, Cu, Pb, and Zn) were measured simultaneously as described by Klučáková and Pavlíková.[53]

Nitrates and phosphates in the water samples were also measured using an in-electrode coulometric titration. In this method, nitrates were electrochemically reduced to ammonium ions,[54] while phosphates were converted to polyphosphoric acid, which were subsequently reduced. A chronopotentiogram was then recorded, where the peak areas were proportional to the nitrate and phosphate concentrations (calculated on the basis of the calibration lines).

Nine water samples (taken from nine sampling locations) were analysed in triplicate at 25 °C (in an air-conditioned laboratory). The data are presented as average values (Tables 1–3).

2.3 Adsorption and desorption experiments with lignite and model aqueous solutions

The adsorption behaviour of lignite was investigated using traditional batch experiments. The solutions were mixed with

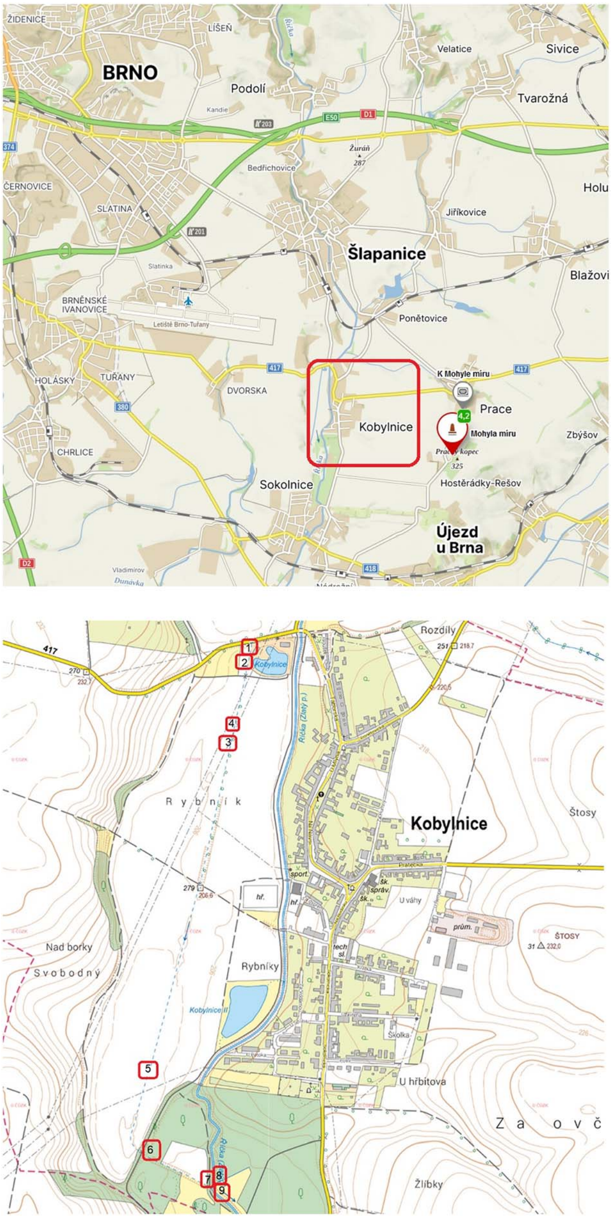

Fig. 1 Location of the Říčka Stream close to Kobylnice (49°8′17 N, 16° 43′55 E) (a) and sampling points (b).

lignite in the ratio of 50 cm^3 to 1 g and stirred until equilibrium. The duration of the equilibration was 24 h, as determined from our previous studies.[53–56] The mixed solutions of metal ions were prepared in the concentration range between 10 and 100 mg dm^{-3} for all metal ions (Cd, Cu, Pb, and Zn). All metals were adsorbed and measured simultaneously. The solutions of nitrate (NO_3^-) were prepared in the concentration range between 5 and 135 mg dm^{-3} (1–30 mg N dm^{-3}), while the solutions of phosphate (PO_4^{3-}) were prepared in the concentration range between 0.8 and 31 mg dm^{-3} (0.2–10 of mg P dm^{-3}). Nitrates and phosphates were adsorbed and measured separately.

Desorption experiments were performed similarly to the adsorption experiments. Adsorbed lignite was mixed with deionized water in the ratio of 50 cm^3 to 1 g and stirred for 24 h. The leached amounts were considered as the mobile fraction, while the residual amounts were considered as the strongly bound fraction.

The concentrations of the metal ions, nitrates and phosphates were measured using an in-electrode coulometric titration (as described in Section 2.2).

All the adsorption and desorption experiments were done in triplicate at 25 °C (in an air-conditioned laboratory). All the solutions and leachates were measured in triplicate. The data are presented as average values. The experimental adsorption isotherms were fitted using eqn (1), as shown in the SI Materials (S1–S4).

2.4 Adsorption and desorption experiments with lignite and real water samples

Lignite was applied to real water samples obtained from the side opening of a canal in the Říčka Stream located in Kobylnice. The adsorption and desorption experiments were performed in the ratio of 50 cm^3 of water sample to 1 g of lignite. After equilibration (24 h), the decrease in the concentrations of the metal ions, nitrates, and phosphates was measured using an in-electrode coulometric titration. The adsorbed lignite was then leached using deionized water and the content of the mobile and strongly bound fractions of the pollutants were determined. The in-electrode coulometric titration was used similarly as previously described.

Table 1 Contents of metal ions, nitrates and phosphates in the water samples (June 6, 2023)

			NO_3^- (mg dm^{-3})		PO_4^{3-} (mg dm^{-3})	
	Cu (μg dm^{-3})	Pb (μg dm^{-3})	Anion	N	Anion	P
1	3.69 ± 0.11	7.96 ± 0.27	69.46 ± 2.35	15.69 ± 0.53	10.44 ± 0.86	3.40 ± 0.28
2	3.56 ± 0.12	7.03 ± 0.21	69.42 ± 2.41	15.68 ± 0.54	10.81 ± 1.03	3.53 ± 0.34
3	3.63 ± 0.18	7.73 ± 0.28	41.61 ± 1.75	9.40 ± 0.39	23.54 ± 1.67	7.68 ± 0.64
4	3.44 ± 0.17	7.26 ± 0.31	48.09 ± 1.22	10.86 ± 0.28	16.09 ± 0.83	5.25 ± 0.27
5	3.43 ± 0.14	7.26 ± 0.12	70.33 ± 2.64	15.89 ± 0.60	13.84 ± 0.93	4.51 ± 0.30
6	3.60 ± 0.17	7.25 ± 0.31	59.52 ± 2.34	13.45 ± 0.53	15.71 ± 0.64	5.13 ± 0.21
7	3.47 ± 0.15	7.26 ± 0.21	67.40 ± 2.69	15.23 ± 0.61	16.84 ± 1.32	5.49 ± 0.43
8	3.47 ± 0.12	7.26 ± 0.22	87.20 ± 3.01	19.70 ± 0.68	13.27 ± 0.84	4.33 ± 0.27
9	3.63 ± 0.13	7.56 ± 0.14	80.83 ± 2.79	18.26 ± 0.63	9.58 ± 0.79	3.13 ± 0.26

Table 2 Contents of metal ions, nitrates and phosphates in the water samples (August 28, 2023)

			NO_3^- (mg dm^{-3})		PO_4^{3-} (mg dm^{-3})	
	Cu (μg dm^{-3})	Pb (μg dm^{-3})	Anion	N	Anion	P
1	34.18 ± 1.61	23.76 ± 1.07	81.12 ± 3.35	18.32 ± 0.76	5.92 ± 0.12	1.93 ± 0.12
2	38.45 ± 1.72	24.20 ± 1.02	88.10 ± 3.41	19.90 ± 0.77	4.00 ± 0.25	1.30 ± 0.08
3	18.31 ± 0.91	28.86 ± 1.14	95.06 ± 3.75	21.47 ± 0,85	16.65 ± 0.52	5.43 ± 0.17
4	19.22 ± 0.94	25.12 ± 0.97	104.57 ± 4.22	23.62 ± 0,95	12.53 ± 0.35	4.09 ± 0.11
5	20.99 ± 1.03	23.62 ± 1.11	112.95 ± 4.64	25.52 ± 1.05	17.33 ± 0.23	5.65 ± 0.08
6	34.15 ± 1.31	24.52 ± 1.22	108.91 ± 4.34	24.60 ± 0.98	14.76 ± 0.12	4.81 ± 0.04
7	30.10 ± 1.20	24.24 ± 0.96	113.93 ± 3,69	25.74 ± 0.83	11.13 ± 0.67	3.63 ± 0.22
8	30.69 ± 1.33	24.79 ± 1.03	84.19 ± 2.21	19.02 ± 0.50	3.23 ± 0.21	1.06 ± 0.07
9	35.04 ± 1.31	20.59 ± 0.91	65.98 ± 2.28	14.90 ± 0.52	6.53 ± 0.40	2.13 ± 0.13

The experiments were performed in triplicate at 25 °C (in an air-conditioned laboratory) and the data were presented as average values.

2.5 Data processing

The experimental data obtained using the procedures described in Sections 2.2, 2.3, and 2.4 were processed as outlined herein. The real water samples (Section 2.2) were always analysed in three measuring vessels and the sample in each vessel was analysed in triplicate. Therefore, nine values were obtained for each real water sample from each sampling site.

The adsorption and desorption experiments (Sections 2.3 and 2.4) were performed in triplicate. Therefore, each batch experiment was performed in three vessels. The sample in each vessel was analysed in triplicate. Therefore, nine values were obtained for the concentration of a pollutant.

The results were presented as an average value ($\bar{x}$) with a standard deviation, s ($\bar{x} \pm s_{\bar{x}}$). The average value was calculated using the well-known equation:

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i = \frac{1}{n}(x_1 + x_2 + \ldots + x_n), \tag{1}$$

The average values were complemented by a relative standard deviation $s_{\bar{x}}$

$$s_{\bar{x}} = \frac{s}{\bar{x}}, \tag{2}$$

where s is the average quadric error, which can be calculated as:

$$s = \sqrt{\frac{\sum_{i=0}^{n} d_i^2}{n-1}} = \sqrt{\frac{n\sum_{i=0}^{n} x_i^2 - \left(\sum_{i-0}^{n} x\right)^2}{n(n-1)}}. \tag{3}$$

The symbol, d_i, represents the deviation of a measured value from the average value:

$$d_i = \bar{x} - x_i \tag{4}$$

The data processing procedure is schematically shown in SI Material S5.

3 Results and discussion

3.1 Analysis of real water samples

Water was sampled on three different dates (June 6, 2023, August 28, 2023, and September 14, 2023). Sampling in July was not feasible because of the dry season and the dearth of water at some sampling locations. The results of the analysed water samples are listed in Tables 1–3. The contents of cadmium and zinc were below the limit of detection on all three sampling dates; therefore, the values are not discussed herein. From the results, there were differences on the individual dates of water sampling. The highest contents of Cu and Pb were detected in August. As mentioned above, sampling in July was not feasible

Table 3 Contents of metal ions, nitrates and phosphates in the water samples (September 14, 2023)

			NO_3^- (mg dm^{-3})		PO_4^{3-} (mg dm^{-3})	
	Cu (μg dm^{-3})	Pb (μg dm^{-3})	Anion	N	Anion	P
1	5.49 ± 0.21	8.52 ± 0.22	114.15 ± 5.07	25.79 ± 1.14	15.69 ± 0.98	5.12 ± 0.32
2	4.61 ± 0.23	8.99 ± 0.41	116.77 ± 4.82	26.38 ± 1.09	5.60 ± 0.28	1.83 ± 0.09
3	7.89 ± 0.33	5.16 ± 0.23	107.30 ± 4.36	24.24 ± 0.98	13.35 ± 0.83	4.35 ± 0.27
4	7.76 ± 0.31	7.51 ± 0.31	113.71 ± 3.68	25.69 ± 0.83	4.63 ± 0.12	1.51 ± 0.04
5	6.54 ± 0.32	9.43 ± 0.37	113.98 ± 5.09	25.75 ± 1.15	6.46 ± 0.34	2.11 ± 0.11
6	6.47 ± 0.29	11.57 ± 0.49	114.06 ± 5.10	25.77 ± 1.15	11.73 ± 0.25	3.83 ± 0.08
7	7.50 ± 0.32	8.26 ± 0.38	108.08 ± 3.98	24.42 ± 0.90	8.69 ± 0.46	2.84 ± 0.15
8	8.15 ± 0.32	9.72 ± 0.34	114.31 ± 4.22	25.82 ± 0.95	2.78 ± 0.18	0.91 ± 0.06
9	5.21 ± 0.19	7.62 ± 0.29	113.66 ± 4.86	25.68 ± 1.10	3.41 ± 0.09	1.11 ± 0.03

Table 4 The adsorption capacity (a_{max}) of lignite for metal ions, nitrates and phosphates, determined based on eqn (2)

		NO_3^- (mg g^{-1})		PO_4^{3-} (mg g^{-1})	
Cu (mg g^{-1})	Pb (mg g^{-1})	Anion	N	Anion	P
8.46 ± 0.40	13.52 ± 0.90	5.92 ± 0.29	1.33 ± 0.07	4.18 ± 0.21	1.36 ± 0.07

because of the dry season and the absence of water at some sampling locations. The dry season partially affected the values measured in August and no rainfall was observed two weeks before sampling. In contrast, the other two sampling excursions (in June and September) were performed after rainfall. The Cu and Pb contents were under the limit (25 μg dm^{-3} for Cu and 14.4 μg dm^{-3} for Pb in surface water according to Act No. 2/1969 Coll., on the Establishment of Ministries and Other Central Government Authorities of the Czech Republic) in June and September (except sampling point number 6 in September), and above the limit in August. Comparably, the results obtained for nitrates and phosphates are different. All the measured concentrations were above the limit (7 mg dm^{-3} for total N in nitrates and 0.2 mg dm^{-3} for total P in surface water according to Act No. 2/1969 Coll., on the Establishment of Ministries and Other Central Government Authorities of the Czech Republic). Differences among the individual sampling points were random without observable trends.

3.2 Adsorption and desorption experiments with lignite and model aqueous solutions

Lignite, the youngest type of coal, is a potential low-cost sorbent for the removal of pollutants from aqueous natural systems and wastewater.[39,56,57] Lignite contains large amounts of humic substances, and it is assumed that humic substances are the main components responsible for the sorption of pollutants on lignite.[39,58] In this study, the effectiveness of lignite as a sorbent for metal ions, nitrates, and phosphates was investigated.[59] Experimental data were fitted using the traditional Langmuir isotherm applicable for the equilibrium between the adsorbed amount and residual concentration in solution, according to eqn (5):[40,60,61]

$$a = a_{max}\frac{bc}{1 + bc}, \tag{5}$$

where a, a_{max}, b, and c are the adsorbed amount, adsorption capacity, adsorption coefficient, and equilibrium concentration in solution, respectively. It is well-known that the isotherm was derived from adsorption and desorption kinetics. Thus, the b coefficient can be considered as the ratio between the constants of adsorption and desorption. Eqn (5) can be linearized to determine parameters a_{max} and b:

$$\frac{1}{a} = \frac{1}{a_{max}b}\frac{1}{c} + \frac{1}{a_{max}}. \tag{6}$$

The curved character of the adsorption isotherms is well-known; therefore, experimental data fitted by eqn (5) are shown in the SI Materials (S1–S4). The initial concentrations of the pollutants in agreement with the results of analysis of real water samples were chosen (Tables 1–3) and measured in an appropriate concentration range using a coulometric analyser. The measured decrease in the concentration of the pollutants provided their equilibrium values as well as the amounts adsorbed per gram of lignite. Their equilibrium concentrations were less than 35% of the initial values, which indicated an effective immobilization of the pollutants using lignite. The adsorbed amounts obtained for the metals were comparable in magnitude (micrograms per gram of lignite). Similarly, the anions from fertilizers were adsorbed in comparable amounts for given concentrations of the solutions. The data were fitted to a Langmuir isotherm (S1–S4). The obtained adsorption parameters are listed in Tables 4 and 5, the adsorption capacities of lignite for the metal ions were higher in comparison with nitrate and phosphate. In contrast, the b parameter of the Langmuir isotherm, which represents the ratio between the rate constants of adsorption and desorption, was high for the anions from fertilizers. The high affinity of the Cu and Pb ions to different sorbents has been reported by many authors (*e.g.*[29,38,45,47–49]). In general, the interactions between lignite and different pollutants have a complex nature given their heterogeneous character. Metal ions, such as Cu and Pb, can be bound to lignite in two main ways: (1) the electrostatic and non-specific interactions of a metal cation with the negative charge on lignite's surface and (2) specific interactions resulting in the formation of complexes and chelates with the functional groups of lignite. While the sorption ability of humic-rich materials for metal ions can be relatively easily understood and explained,[38,53,55,56,58,62,63] their affinity to anions is not fully clear.[7,28,50,52,58] Anions can be probably bound by ion exchange

Table 5 The ratio between adsorption and desorption rate constants (b) for the adsorption of metal ions, nitrates and phosphates on lignite, determined based on eqn (2)

		NO_3^- (dm^3 g^{-1})		PO_4^{3-} (dm^3 g^{-1})	
Cu (dm^3 g^{-1})	Pb (dm^3 g^{-1})	Anion	N	Anion	P
33.44 ± 1.26	13.62 ± 0.92	54.43 ± 2.71	240.94 ± 0.61	43.73 ± 2.16	134.08 ± 6.62

with hydroxyl ions through hydrogen bonding, which involves the hydrogen atoms of functional groups present on lignite's surface, and through metal bridges formed with oppositely charged metal ions present in lignite.[58,64–66]

Lignite (similar to other humic-rich materials) is heterogeneous, containing many different constituents; consequently, it is able to more or less bind a broad range of pollutants. Its interactions with pollutants can result in water-soluble and water-insoluble complexes with different bond strengths. Thus, pollutants can exist on lignite in several fractions, differing in their degree of immobilization and migration ability. Consequently, the various forms of ligands binding on lignite's surface can probably participate both in irreversible and reversible sorption. Simple desorption experiments, which can be realized by leaching pollutants from lignite into water, provide two fractions of the studied pollutants: free mobile particles, which are able to leach from lignite and migrate into environmental water, and pollutants immobilized on lignite's structure and as such were not leached from the adsorbent and remained bound.

In Fig. 2, the average adsorption effectiveness and the contents of the leachable and strongly immobilized pollutants are shown. The highest adsorption effectiveness was for copper, while the lowest value was for nitrates. However, all the observed efficiencies were similar, within the range of 75–85%. These efficiencies were a little lower when compared with the adsorption of metal ions and nitrates on humic acids[53–55] due to the occurrence of other constituents in lignite, lowering the content of humic substances in lignite. On the other hand, lignite in the natural state can be considered as a cost-effective adsorbent suitable for the removal of pollutants from natural systems, whereas the use of lignitic humic substances for these purposes requires isolation from lignite, which is associated

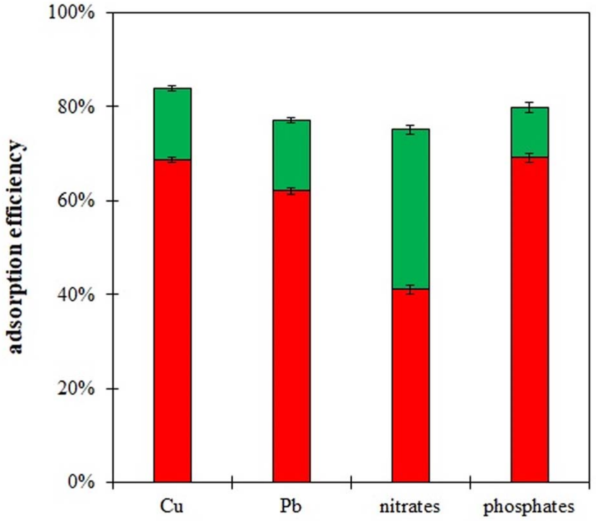

Fig. 2 Adsorption efficiency of lignite for metal ions, nitrates, and phosphates (model solutions). Data are represented as bars, divided into mobile (leachable) fraction (green) and strongly bound (immobilized) fraction (red).

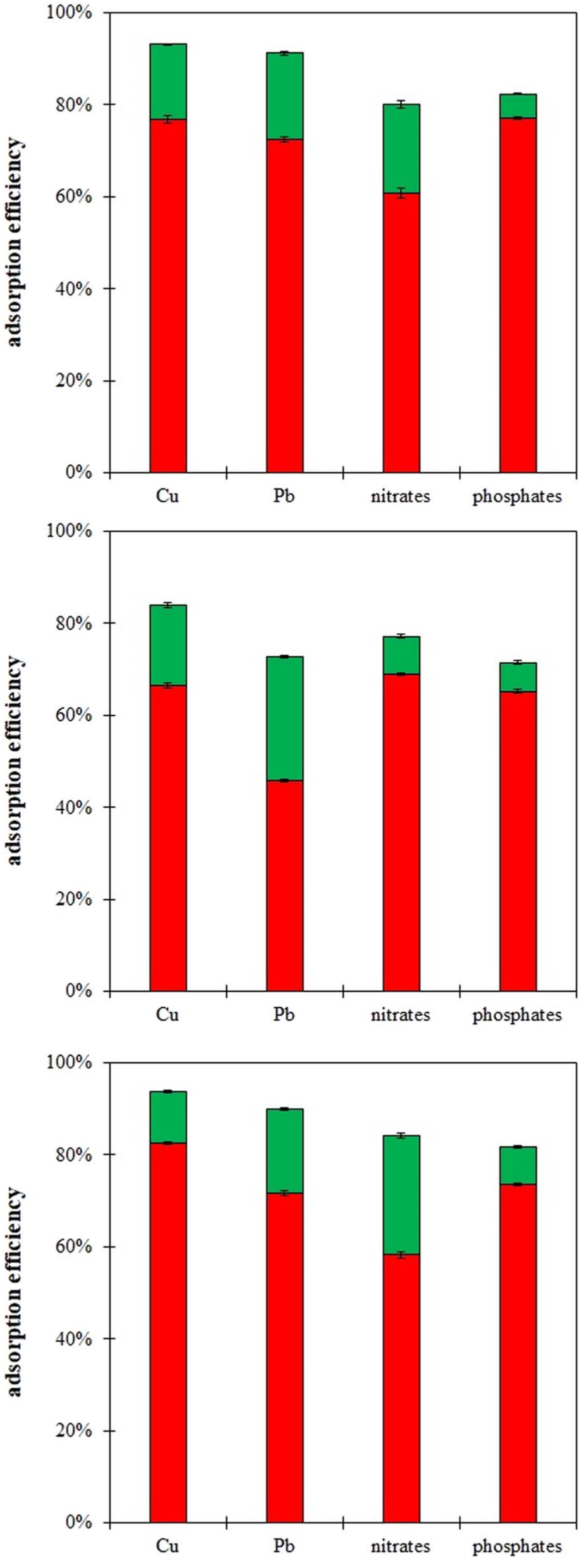

Fig. 3 Adsorption efficiency of lignite for metal ions, nitrates, and phosphates (real water samples): water sampled in June 2023 (a), August 2023 (b), and September 2023 (c). Data are represented as bars, divided into mobile (leachable) fraction (green) and strongly bound (immobilized) fraction (red).

with increased production costs. The results obtained in this part of our study showed that lignite was able to remove significant amounts of metal ions, nitrates, and phosphates from the water and its adsorption capacity was sufficient for the contents of pollutants determined from the studied Říčka Stream.

The highest content of leachable fraction was observed for nitrates, while the lowest fraction was observed for phosphates. The leachable fractions for both metal ions were comparable. However, the majority of the adsorbed pollutants remained bound on lignite in all cases (Cu, Pb, nitrates, and phosphates). This observation means that the application of lignite can decrease the contents of pollutants, as well as their toxicity and bioavailability.

3.3 Adsorption and desorption experiments with lignite and real water samples

Lignite was applied for removing pollutants from the real water samples analysed in first part of this study (Tables 1–3). It was found that lignite was able to adsorb the majority of pollutants from the water samples (see Fig. 3). Its effectivity exceeded 70% for all the water samples and pollutants. No significant differences were observed for the individual sampling locations. The highest efficiency was determined for the adsorption of Cu (93–94%) and Pb (90–91%) in water sampled in June and September. The lowest efficiency was observed for Pb and phosphates in water sampled in August (71–73%). The efficiency was lowest for all the pollutants and all water sampled in August (in comparison with July and September). It is logical to assume that water sampled on different days (and months) can result in different compositions of the samples and generally different results. Water sampled in August evinced a much higher heavy metal pollution in comparison with July and September. The contents of nitrates and phosphates were comparable with the other sampling dates. Therefore, two factors can affect the adsorption efficiency. The first factor is that the adsorption efficiency is dependent on the initial concentration of the pollutant and decreases as concentration increases. The second factor accounts for the presence of other pollutants in real water samples. As described previously (*e.g.*[53,67]), the adsorption efficiency of a mixed solution is usually lower in comparison with a solution containing only one pollutant. The reasons for this observation are an increase in ionic strength and the associated salt effect (which can both suppress and support interactions on the surface of lignite), as well as competition among the pollutants. Other important influences can be the concentration of pollutants, which is affected by weather conditions and the amount of water in the stream. The weather conditions and individual water sampling data are presented in Table 6. From the obtained results, the rainfall before sampling in June can account for the lower pollutant content of the samples than when sampling was done in August and September. In contrast, higher temperatures in August resulted in a reduced amount of water in the stream, which concentrated the pollutants. This observation was mainly the case for the metal ions, which were several times more concentrated in August when compared with the values determined in June. Additionally, this hypothesis can be supported by the low amount of water in stream, which thwarted water sampling in July. It is interesting that the highest contents of nitrates in water sampled in September were removed with the highest efficiency.

As described above, pollutants can be bound to an adsorbent, such as lignite, with different strengths due to the different binding sites in the structure and non-specific interactions. A part of the bound pollutants can leach into water and migrate into the surrounding natural systems (soils and sediments). This fractionation of adsorbed pollutants results in freely mobile (leachable) and immobilized (strongly bound) particles, as shown in Fig. 3. However, the desorption of the monitored metals was different. While the leachability of Cu increased slightly in August and decreased in September (in comparison with June), the increase of Pb leachability in August was much higher than that of Cu (results obtained for June and September were practically the same). This discrepancy between both metals was probably connected to a decrease in the adsorption efficiency of lignite for Pb in the water sampled in August. The lowest leachable fraction of the adsorbed amount was for phosphates (5–8%). The complexes of phosphates formed with lignite can be considered stable and their adsorption to lignite can considerably reduce their toxicity and bioavailability. In contrast, nitrates showed a different behaviour; their leachability in the August sample was very low (∼8%) in comparison with the June (∼19%) and September (∼25%) samples. Although the application of lignite achieved the lowest adsorption efficiency in August for nitrates, its decrease was not too marked for some of the other pollutants (Cu, Pb, phosphates). Therefore, it seems that the dry weather in August and the related low content of water in stream had a different effect on the bioavailability of nitrates. As shown in Fig. 4, the content

Table 6 Weather and circumstances for water sampling

	Temperature	Rel. humidity	Rainfall (48 h)	Ref.
June 6, 2023	15–22 °C	78%	17 mm	https://www.meteoblue.com/cs/po%C4%8Das%C3%AD/archive/era5/kobylnice_%c4%8cesko_3073472?fcstlength=1m&year=2023&month=6
August 28, 2023	18–30 °C	70%	1 mm	https://www.meteoblue.com/cs/po%C4%8Das%C3%AD/archive/era5/kobylnice_%c4%8cesko_3073472?fcstlength=1m&year=2023&month=8
September 14, 2023	15–23 °C	72%	0 mm	https://www.meteoblue.com/cs/po%C4%8Das%C3%AD/archive/era5/kobylnice_%c4%8cesko_3073472?fcstlength=1m&year=2023&month=9

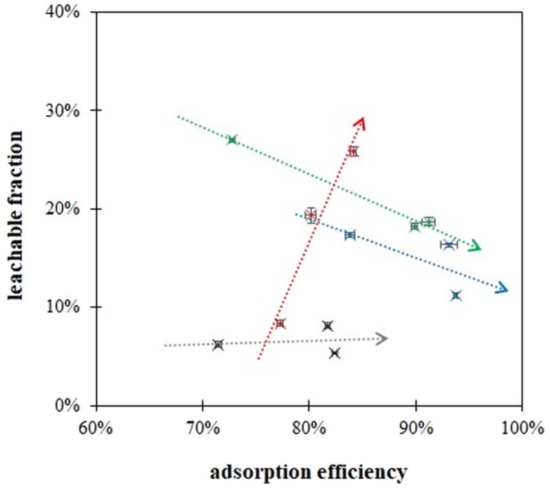

Fig. 4 Dependence of the leachable fraction on the adsorption efficiency of lignite for the real water samples: Cu (blue), Pb (green), nitrates (red), and phosphates (grey).

of the leachable fraction (and in a sense the stability of the formed complexes and bioavailability of pollutants) was more or less dependent on the adsorption efficiency. While this dependence decreased for metal ions and only increased a little for phosphates, its increase for nitrates was strong (in comparison with other pollutants); however, it is not easy to explain this discrepancy. We assume that an equilibrium between the leachable and strongly bound fractions can be established, resulting in a fraction where nutrients were available and the other fraction remained immobilized. It is widely accepted that lignite contains high amounts of humic substances, which are similar to the constituents of organic matter in soil. A fraction of nutrients can be immediately available for plants, and another fraction comprises a reservoir from which nutrients can be converted to a leachable form that is available for release.

4. Conclusions

The study was divided into three sections: the analysis of real water samples, the testing of lignite as a sorbent for the removal of pollutants, and the application of lignite for real water samples. In the first section, the samples were analysed for metal ions and nutrients originating from fertilizers. The Cu and Pb contents were at values below the limit in June and September and above the limit in August (probably due to the dry season). Cd and Zn were below the limit of detection for all three sampling dates. All the measured concentrations of nitrates and phosphates were above the limit. The testing of lignite as a natural, cost-effective adsorbent rich in humic substances provided a high-efficiency removal strategy for all the monitored pollutants. The majority of the adsorbed pollutants remained immobilized and only low amounts of adsorbed pollutants were leached into the water. The application of lignite for the real water samples confirmed that all the monitored pollutants can be effectively immobilized onto lignite; its effectivity exceeded 70% for all the water samples and pollutants. The behaviour of nitrates differed from the other pollutants; their mobile fraction strongly increased with the adsorption efficiency and their leachability was higher in comparison with other pollutants. However, the equilibrium concentrations of nitrates after adsorption as well as their leachable form were under the limit applicable in the Czech Republic.

Author contributions

M. Klučáková and M. Pavlíková conceived the overall article framework; M. Klučáková and P. Závodská performed literature reviews; P. Závodská, M. Pavlíková, L. Buršík, and V. Sobotková sampled and analysed the water samples; P. Závodská performed the adsorption and desorption experiments; and M. Klučáková processed the experimental data and wrote the manuscript.

Conflicts of interest

The authors declare that no competing financial interests exist.

Data availability

Data will be made available on request.

Supplementary information is available. See DOI: **https://doi.org/10.1039/d5va00205b**.

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