Sorption properties of low calorific value Greek lignites: Removal of lead, cadmium, zinc and copper ions from aqueous solutions

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A R T I C L E   I N F O

A B S T R A C T

The removal of metal ions (Pb, Cd, Zn, and Cu) from spiked aqueous solutions using four lignite samples (TH2, TH7, MT2, and MT8) of different quality, from different areas in Greece, was investigated. Cation exchange capacity, humic and fulvic acid content, and the BET specific surface area of the samples were determined, proximate and ultimate analyses were conducted and the mineralogy of their low temperature ash was studied. Equilibrium and kinetic studies were performed in batch conditions. Competitive adsorption of the four elements examined was also investigated. It was observed that the four lignite samples were considerably effective in removing Pb, Cd, Zn, and Cu ions from aqueous solutions, with the sample MT2 being the most effective. Among the elements, Pb appeared to have the strongest affinity based on a mass uptake by lignite samples. The same behaviour was observed during the competitive adsorption experiments. Kinetic experiments proved that, in all cases, equilibrium was achieved within 45 min. Sorption isotherm studies were conducted by varying the initial concentration of the elements. MATLAB software was used to fit experimental data to Langmuir and Freundlich equations. The data were better fitted to the Langmuir equation. Attempt was made to correlate the adsorption behaviour of the lignite samples with the mineralogy of their low temperature ashes and their content in humic and fulvic acids.

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1. Introduction

Environmental pollution by heavy metals has become an ecotoxilogical hazard of prime interest and increasing significance. Heavy metal ions are released into the environment in a number of different ways and because of their accumulation in living organisms form a serious and complex problem that has been a focus of attention all over the world.

As far as surface and groundwater are concerned, heavy metals can be considered among the chief pollutants. The concentrations of these toxic elements have to be reduced to meet the ever increasing legislative standards. The conventional techniques for the removal of heavy metals include ion exchange, filtration, electrolytic or liquid extraction, chemical precipitation, reverse osmosis, and membrane techniques [1–7]. In several cases the above mentioned techniques are either economically unfavorable or technically complicated making the arena ripe for new methods for treatment of metals contaminated water. Among new methods, the utilization of lignite, for the treatment of wastewater containing heavy metals, is gaining more attention as a simple, effective and economical means of pollution remediation. The mechanism by which metal ions are sorbed onto low rank coal is a matter of considerable debate. Different

studies have reached to different conclusions, and theories related to the matter include ion exchange, surface adsorption, complexation, chemisorption, and adsorption–complexation. Among these theories, ion exchange appears to be the most prevalent mechanism [8]. Although the adsorption capacity of low rank coals is lower in comparison to that of synthetic ion exchange materials, the fact that they are plentiful and inexpensive makes them an attractive and inexpensive option for the removal of metals.

In Greece, there are several lignite deposits of various sizes, with low calorific value that can not be utilized for power generation [9–12]. Such lignites are rich in mineral matter and therefore possess low calorific value. Several studies [13–16] have been undertaken on the non-electric uses of lignite, with waste water treatment to be among the promising of them.

The aim of the present work is to investigate the possibility of using four Greek lignites, rich in mineral matter, with low calorific value, for the removal of metal ions from waste water. In this context, experiments of removing Pb(II), Cd(II), Cu(II), and Zn(II) ions from spiked aqueous solution were conducted in batch mode. The effects of contact time and of metal initial concentration on the kinetics of sorption capacity of the lignite samples were studied. The simultaneous sorption of the above metals was also investigated. The mineralogy of the low temperature ash of the samples was studied in order to investigate whether the inorganic matter contributes to the sorption properties of the samples. Experimental data, produced by sorption isotherm studies, were fitted to the

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Langmuir and the Freundlich equations in order to decide which model describes better the sorption process.

2. Experimental

2.1. Sorbent characterization

The four lignite samples TH2, TH7, MT2, and MT8 were obtained from different basins in Greece after an extensive drilling campaign. They were coded after the location: Thessaly, central Greece (code TH), Macedonia and Thrace, northern Greece (code MT). The lignite deposits were chosen because they can not be exploited for power generation and because the content of clay minerals in the mineral matter is high and detailed information about the samples is given in [17].

The samples were crushed (Ø < 1 mm), dried at 45 °C for 24 h and subsequently pulverized to pass through the 0.250 mm sieve The proximate and ultimate analysis were conducted according ASTM D 3173-87 and ASTM D 3176-89 standards, respectively, and calorific value was measured using an automatic calorimeter (Leco, model A300). The cation exchange capacity of the samples was determined using a Kjeldahl microsteam apparatus after saturation with ammonioum acetate [18]. The humic and fulvic acid contents of the lignite samples were determined according to the method described by Swift [19]. The specific surface area of the samples was determined with the Nova 2200 apparatus (QuantChrom) according the BET method.

Mineralogical components were determined by X-ray diffraction (XRD) using a Siemens D500 XRD instrument. The data were obtained at 35 kV and 35 mA, with a graphite monochromator, using CuKα radiation. The qualitative evaluation of the data was done with the Software Diffrac Plus from SOCABIM. The quantitative analysis was carried out by the Rietveld Method [20].

2.2. Sorption experiments

2.2.1. Sorption kinetics

Batch experiments were conducted, at room temperature, in 400 mL plastic beakers, under continuous stirring. In each case 1 g of air dried lignite and 100 mL of metal solution were used. The metal solutions used for the batch experiments were prepared using analytical grade nitrate salts of the corresponding elements: $Pb(NO_3)_2$, $Cd(NO_3)_2 \cdot 4H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Cu(NO_3)_2 \cdot 3H_2O$ (puriss p.a. quality, FLUKA). Kinetic experiments were carried out with solutions of initial concentration of 1000 ppm for all elements. After different periods of contact time (5, 10, 20, 45, 60 and 120 min) the aqueous phase was withdrawn and filtered to determine the residual metal concentration. The analysis of metals in solutions that were produced after treatment of the lignite samples with deionized water showed that there was no leaching from the sorbents.

The residual concentration of the elements in the aqueous phase was analyzed by Flame Atomic Absorption Spectroscopy. Air/acetylene flame was used and wavelengths of 283.3, 228.8, 213.9, 324.8 nm were used for the elements Pb, Cd, Zn, and Cu respectively. The spectrometer used was the "Analyst 100" model by PerkinElmer.

2.2.2. Sorption isotherms

Sorption isotherm studies were conducted for sample MT2, which was proved to be the best adsorbent, by varying the initial concentration of the elements from 10 to 1000 ppm (10, 50, 100, 300, 500, 700, and 1000 ppm). The sorption conditions were kept the same as in sorption kinetics and 45 min was chosen as contact time. This time was chosen because in previous kinetic experiments it was proved to be sufficient for all elements to reach equilibrium.

Table 1
The lithotype, the composition % of ash, volatile matter, fixed carbon, C, H, N, O, S, humic and fulvic acids (H/F a), the calorific value (Cal. value) in MJ/kg, the cation exchange capacity (CEC) in meq/100 g and the surface area (SA) in m^2/g, for the lignite samples investigated (in dried form).

Properties	Lignite samples			
	TH2	TH7	MT2	MT8
Lithotype	Peat with clay particles	Xylite rich lignite	Mixed peat clay-rich	Matrix lignite
Ash (%)	59.34	17.27	42.18	61.41
Vol. Mat. (%)	66.29	56.94	67.86	61.91
Fixed C (%)	33.71	43.06	32.14	38.09
C (%)	55.13	65.82	61.58	56.52
H (%)	5.73	5.03	5.35	6.41
O (%)	34.59	25.08	25.69	29.31
N (%)	2.79	1.52	2.25	0.69
S (%)	1.83	2.55	5.13	7.07
H/F acids (%)	7.99	28.85	32.35	2.78
Cal. value (MJ/kg)	18820	25461	23560	17598
CEC (meq/100 g)	88.1	103.0	71.8	47.3
Surf. area (m^2/g)	13.99	3.62	4.20	23.84

The residual concentration of the elements in the aqueous phase was analyzed by Flame Atomic Absorption Spectroscopy.

2.2.3. Competitive sorption

Competitive adsorption of elements on MT2 was investigated using a solution which contained 100 ppm of each element. The sorption conditions were kept the same as in sorption kinetics and 45 min was chosen as contact time. This time was chosen because by the kinetic experiments it was proved to be sufficient for all elements to reach equilibrium. The residual concentration of the elements in the aqueous phase was analyzed by Flame Atomic Absorption Spectroscopy.

All experiments were carried out in duplicate.

Initial pH and pH throughout the experiments were determined using a pH meter (model InolabLevel1, by WTW).

3. Results and discussion

3.1. Sorbent properties

The lithotype of the samples and the results of their proximate and ultimate analysis are reported in Table 1. In the same table are reported the humic and fulvic acids content of the samples, their calorific value, their cation exchange capacity and their surface area. The mineralogy of the low temperature ashes is given in Table 2.

The results show that, except sample TH7, the samples have a high content in mineral matter. The mineralogical analysis of the low temperature ash of the samples shows that the sample with the highest content in clay minerals (Kaolinite and Muscovite/Illite) is MT8. This sample is the one with the lowest humic and fulvic acids content and the lowest cation exchange capacity while TH7, the sample with the lowest content in ash, possesses the highest

Table 2
The mineralogy of the low temperature ashes.

Minerals (%)	Lignite samples			
	TH2	TH7	MT2	MT8
Kaolinite	26.6	19.2	24.0	53.2
Calcite	1.5	0.5	2.1	2.3
Bassanite	2.8	27.9	9.5	3.0
Anhydrite	0.2	4.7	7.1	1.4
Quartz	12.4	15.0	15.7	2.8
Pyrite	0.2	1.5	0.8	1.4
Plagioclase	7.8	1.7	7.6	2.4
Muscovite/Illite	48.5	29.5	33.2	33.7
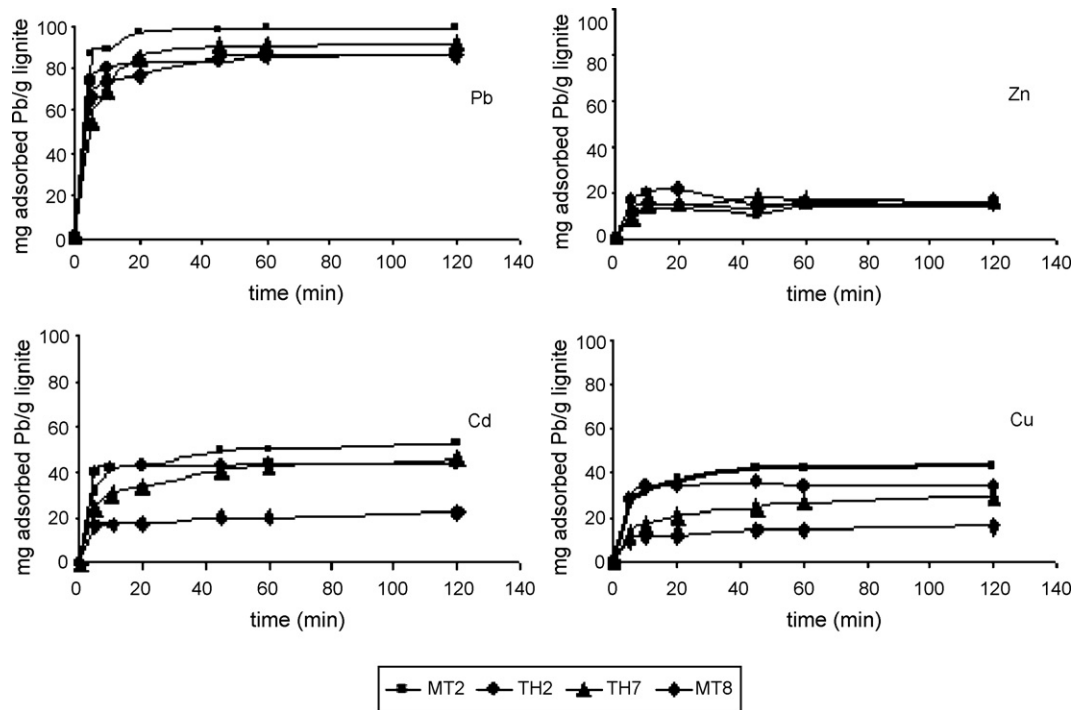
Fig. 1. Adsorption kinetics of metal ions by lignite sample, in single systems. Experimental conditions: initial metal concentration 1000 ppm, amount of lignite 1.0 g, volume of solution 100 mL, pH 4–5, temperature 25 °C.

cation exchange capacity. Sample MT2 has the highest content in humic and fulvic acids and MT8 is the one with the highest surface area.

The above mentioned observations imply that the sorption properties of the samples should be attributed to the organic matter rather than the mineral matter, since sample MT8 that has the highest content (86% in the low temperature ash) in clay minerals has the lowest cation exchange capacity.

3.2. Sorption experiments

3.2.1. Sorption kinetics

3.2.1.1. Effect of contact time. The effect of contact time on metal sorption kinetics by lignite samples is illustrated in Fig. 1. In all cases high adsorption rates are observed at the beginning and gradually plateau values are reached. The equilibrium time observed for Pb and Cu is 45 min for all lignite samples. Zn equilibrium time was 20 min for all samples, while Cd equilibrium time was 45 min for sample MT2 and 10 min for the rest of the samples. Sample MT2 appeared to be the most effective adsorbent. Among the elements, lead appeared to have the strongest affinity (Fig. 1) based on a mass uptake by lignite samples, followed by Cd and Cu while Zn proved to be the one with the poorest affinity. The order of adsorption affinity for the four elements has been attributed, by different authors [21–24], to their ionic properties such as electronegativity, ionic potential and ionic radius.

3.2.1.2. Effect of initial concentration. The percentage of metal adsorbed on the MT2 lignite sample as a function of the initial concentration is presented in Fig. 2. The amount of Cu, Cd, and Zn adsorbed on the lignite sample increased with the increase of initial concentration up to 100 ppm. After this concentration no increment is observed, suggesting saturation for the active points on the lignite sample. When the initial concentration reaches 1000 ppm less than 50% of the metal added is adsorbed. This trend is not observed for Pb, for which, the lignite sample appears to have the highest maximum

adsorption capacity. It was observed that with initial concentration 1000 ppm the amount of Pb adsorbed on the lignite was 98.5% of the metal added. (Fig. 2)

3.2.1.3. Influence of pH. It is well known that pH is among the controlling factors in the sorption process. In the present work, pH was measured in the beginning and throughout the experiments. In all cases pH was found between 4 and 5. Since this pH range is reported by several researchers [6,7,25,26] as optimum for the sorption of metals by low rank coal, no pH adjustment was considered necessary.
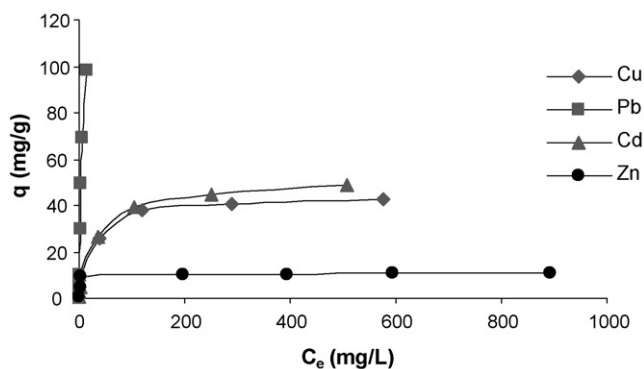
3.2.2. Sorption isotherms

Saturation of the active points in the lignite sample is achieved for initial concentrations lower than 1000 ppm (Fig. 2). As shown in Fig. 3 for all metals studied, sorption isotherms may be considered of H or L type according to the classification of Giles et al. [27], indicating that MT2 shows high affinity for the metals studied.

To analyze the experimental equilibrium data and to obtain the maximum adsorption capacity of the lignite sample, the Langmuir [28] and Freundlich [29] models have been tested
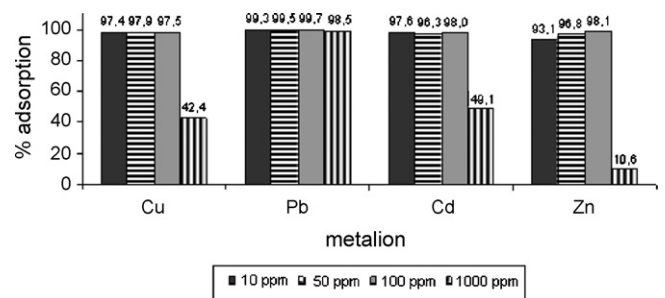
Fig. 2. Adsorption of metal ions, on MT2 for different initial metal concentration, in single systems. Experimental conditions: amount of lignite 1.0 g, volume of solution 100 mL, pH 4–5, temperature 25 °C, contact time 45 min.

Fig. 3. Isotherms of the four metals sorption by MT2 lignite sample. Experimental conditions: amount of lignite 1.0 g, volume of solution 100 mL, pH 4–5, temperature 25 °C, contact time 45 min.
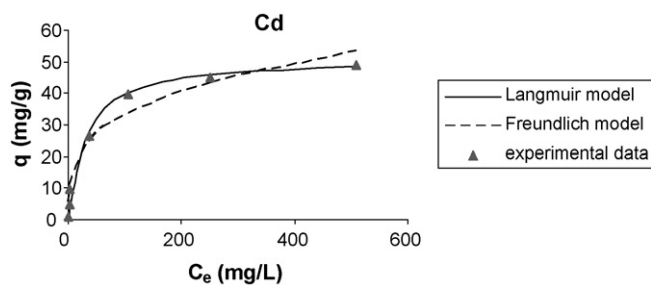
Fig. 4. Sorption isotherms for Cd. Lines represent predicted data by Langmuir and Freundlich model and symbols correspond to experimental data.

The equations used were:

$$q = \frac{q_{max}bC_e}{(1 + bC_e)} \quad \text{(Langmuir)} \tag{1}$$

$$q = KC_e^{1/n} \quad \text{(Freundlich)} \tag{2}$$

where q is the amount of metal ion adsorbed per unit mass of lignite, C_e is the cation concentration at equilibrium, q_{max} is the maximum adsorption capacity; K is related to the adsorption capacity and b, n are constants related to adsorption intensity. For a non linear regression, MATLAB software was used. In Fig. 4 both Langmuir and Frundlich fits for Cd, as an example, are presented for comparison. Experimental data of the present work were better fitted to the Langmuir equation than the Freundlich one, since the correlation coefficient calculated for the Langmuir equation was higher than that for the Freundlich equation (Table 3). This suggests that the sorption of the metals by the lignite sample follows the Langmuir model and that the adsorption process could be described by the formation of monolayer coverage of the adsorbate on surface of the adsorbent. The maximum adsorption capacities calculated by the Langmuir equation were 150.1, 51.48, 42.68, and 10.71 mg/g for the elements Pb, Cd, Cu, and Zn respectively (Table 3). These adsorption capacities are in accordance with those of the literature: for Cd, Cu, and Zn they are equal or higher than those reported elsewhere [3,6,7,25,26] while for Pb, only one sample is reported to

Table 3
Langmuir and Freundlich constants from the metal adsorption isotherms at 25 °C, in single systems.

	Q_{max} (mg g^{-1})	b (L mg^{-1})	r^2	K	n	r^2
Pb	150.1	0.125	0.997	21.04	1.723	0.992
Cd	51.48	0.033	0.974	8.561	3.4	0.956
Cu	42.68	0.064	0.987	10.78	4.327	0.868
Zn	10.71	0.755	0.832	5.13	8.54	0.715

Table 4
The χ^2 values calculated for both models and each element. (in the present study, $\chi^2_{0.05} = 12.592$).

	Langmuir	Freundlich
Cu	4.857	12.069
Pb	4.701	5.633
Cd	10.772	8.448
Zn	4.243	6.776
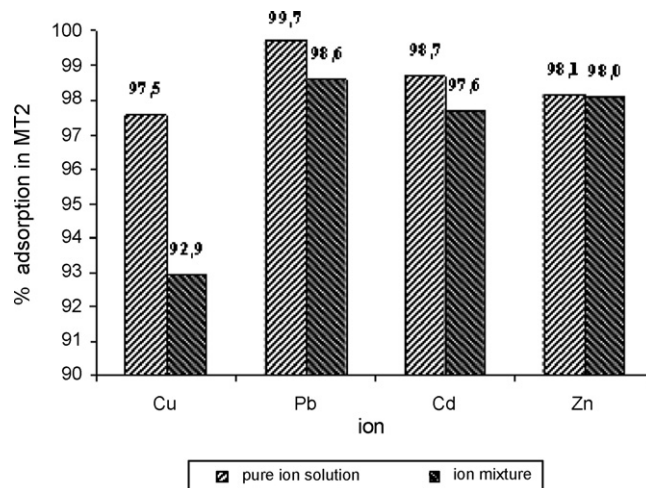
Fig. 5. Competitive metal adsorption on MT2. Experimental conditions: initial metal concentration 100 ppm, amount of lignite 1.0 g, volume of solution 100 mL, pH 4–5, temperature 25 °C, contact time 45 min.

have higher adsorption capacity [26]. Furthermore the chi - square goodness of fit test was performed to check the models tested here. For the present study and for a 5% significance level, χ^2_α was 12.592. On Table 4 the χ^2 values calculated for both models and each element are presented. In all cases the experimental data proved to fit both Langmuir and Freundlich equations.

3.2.3. Competitive adsorption

The results of the competitive adsorption experiments are illustrated in Fig. 5. Among the elements studied, Cu appeared to be the only element whose adsorption is considerably influenced by the presence of the other elements. The elements Pb, Cd, Zn, exhibit low sensitivity to the presence of competitive adsorbates, with Zn being less sensitive than the others. During competitive adsorption, lead appeared to have the strongest affinity based on a mass uptake by the MT2 lignite sample as it did during the non competitive adsorption.

4. Conclusions

The four lignite samples examined in this study were considerably effective in removing Pb, Cd, Zn, and Cu ions from aqueous solutions.

From a certain correlation of the properties determined for the lignite samples, with their adsorption behaviour, it is noted that sample MT2, with the highest content in humic substances, appeared to be the most effective adsorbent while sample MT8, with the highest content in inorganic substances and the lowest in humic substances, was proved to have the poorest behaviour as adsorbent. Consequently, this adsorption behaviour of the samples can be attributed to the humic substances rather than the inorganic substances.

The kinetic experiments proved that equilibrium was achieved within 45 min for all elements. The equilibrium time observed for

Pb and Cu is 45 minutes for all lignite samples. Zn equilibrium time was 20 minutes for all samples, while Cd equilibrium time was 45 minutes for sample MT2 and 10 minutes for the rest of the samples. The behaviour of the elements with Pb having the strongest affinity, and Zn the poorest one is in accordance with literature [3,6,25,30,31].

Experimental data of the present work were better fitted to the Langmuir equation than the Freundlich one, suggesting that the adsorption process could be described by the formation of monolayer coverage of the adsorbate at the surface of the adsorbent.

Lignite samples studied are a raw material of low cost, plentiful in Greece, with high metal uptake levels, both individually and in competition. This combination and the fact that no pH adjustment is required to improve their performance as sorbents, make them a promising material for metal contaminated wastewater treatment.

Additional work is required to identify the mechanism of the sorption process, to study the sorption of metals in other forms, than nitrates, and to optimize the whole process. Desorption experiments should also performed to check whether metals can be easily desorbed in order to recycle the sorbent. These are points that need to be investigated in order to design pilot scale or field scale projects.

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