

The Adsorption of Lead Using Altered Coals

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Abstract. The main aim of the paper is to evaluate altered bituminous coals as immobilization agents for removing heavy metals from aqueous solutions. Lead was used as model metal. As a comparison basis, adsorption of lead on humic acid and commercial activated carbon were used. Adsorption isotherms have been plotted ($R^2 \approx 1$), the adsorption process was well described by the Langmuir adsorption isotherm. Adsorption capacity for altered bituminous coal has been calculated. The influence of coal grain size, pH and technique (batch vers. continuous-flow) has been investigated. In addition, roles of coal surface area and amount of humic acid presented in coal are described.

Keywords: altered coal, adsorption, lead

1. Introduction

Active carbons are effective adsorbents for the removal heavy metals from wastewater. Each carbonaceous material can be converted into adsorbent with varying surface area and pore structure after an appropriate thermal treatment followed physical or chemical activation. Therefore, the high cost of those adsorbents limits their utilization.

The ability of bituminous coals to form stable complexes with metal ions has long been recognized. This property has been successfully utilized to estimate the concentration of acidic functional group present in coal. Although the cation exchange capacities of bituminous coals are significantly lower in comparison to active carbons, the substantially lower cost of the bulk material indicated great potential for the utilization of bituminous coals as a means to remove a range of metals from solution.

In this study, the ion exchange properties of bituminous coals from Ostrava- Karvina district were evaluated to explore its viability as a remediation agent for removing heavy metals from aqueous solutions. Lead was used as model metal. The effects of pH and grain size of the coal on the adsorption were investigated. In addition, roles of coal surface area and amount of humic acids presented in coal are described. Batch and continuous- flow systems were used.

2. Experimental Methods

2.1. Adsorbents

Three natural bituminous coal samples from Upper Silesian Coal Basin were investigated: oxidative altered coal (denoted as OA), thermally altered coal (TA) and “normal”, non-altered bituminous coal (BC). When received, the as-mined coal samples were ground and passed trough several sieves. We obtained various grain sizes and then stored them inside sealed plastic containers. In this study we used these sizes – 0.06-0.25 mm and 0.8-1.0 mm. In addition, as a comparison basis, humic acid (HOA) and commercial activated carbon from MChZ Hrušov (AC) were studied. Sample of humic acid was obtained from oxidative altered coal OA by its leaching with aqueous NaOH ($\approx 10\%$) and subsequent precipitation of alkali-soluble portion by HCl ($\approx 1M$).

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2.2. Chemicals

The chemical used in this study was lead nitrate. The solution pH was controlled by addition HCl and NaOH. All the solutions were made in distilled water. Analytical grade chemicals were used.

Table 1: Proximate analyses and surface areas of samples [1]

Sample	Humic acid %	C %	H %	(O+S) %	-COOH <i>mmol/g</i>	N	S ^{BET} m ² /g
OA	30	76.6	4.1	17.5	1,5	1.8	1.3
HOA	100	71.2	4.2	23	3,4	1.6	1.0
BC	0	85.1	4.7	8.7	n.d.	1.5	1.5
TA	0	88.2	3.9	6.5	n.d.	1.3	9.3
AC	0	> 99	n.d.	≈ 0.5	n.d.	n.d.	1190

n.d. – not determined

2.3. Batch Experiments

About 0.5 g of dried sample was added to 50 mL of a given metal solutions of known concentration varying in the range 10 - 0.1 mmol/l and occasionally shaken. The pH value of each suspension was adjusted by adding either NaOH or HCl; the pH of the solution was measured using a combination single-junction pH electrode with Ag/AgCl reference cell and MS 22 pH meter (LP Prague). Adsorption equilibration took about 6 days, as deduced from previous measurements [2], however, in this study, at least 12-day period of contact time was used. Then, the coal sample was removed by filtering through paper filter. The metal concentration of the filtered solutions was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES).

2.4. Flow Experiments

Procedure for breakthrough curve determination

1. 5 l of adsorbate solution of desiderative concentration was prepared,
2. Altered coal (OA) was poured into the column,
3. The adsorbate solution was introduced into the adsorbent column by burette and contact time was determined,
4. The column effluent was collected at regular intervals,
5. Collected samples were analysed on ICP-AES, the amount initially taken minus the amount found after the passage through the column gave the amount of Pb²⁺ retain by coal.

3. Results and Discussion

3.1. Effect of pH

The pH in the solutions is a relevant factor that affects adsorbed amount of the ions, an increase in the adsorption capacities am was generally found with rise in the pH (Figure 1). In general, such a behaviour is explained by a shift in dissociation equilibrium of the acidic (carboxyl) groups on coal surface with a change in the pH [3-6]. Evidently, this is the case of the HOA and the OA samples with high contents of the carboxylic groups (cf. Table 1) and proving at least twofold increase in the ion adsorption capacity when the pH rises from 3 to 5.

3.2. Effect of Particle size

Because the mill of solid materials is expensive, effect of particle size was investigated. We used three different diameters of coal – 0.06-0.25, 0.25-0.8, 0.8-1.0 mm. Fig. 2 shows the effect of particle size, adsorption isotherms were plotted. Higher adsorption for smaller particle size seems due to larger surface area per unit mass of coal, but the difference is not too high.

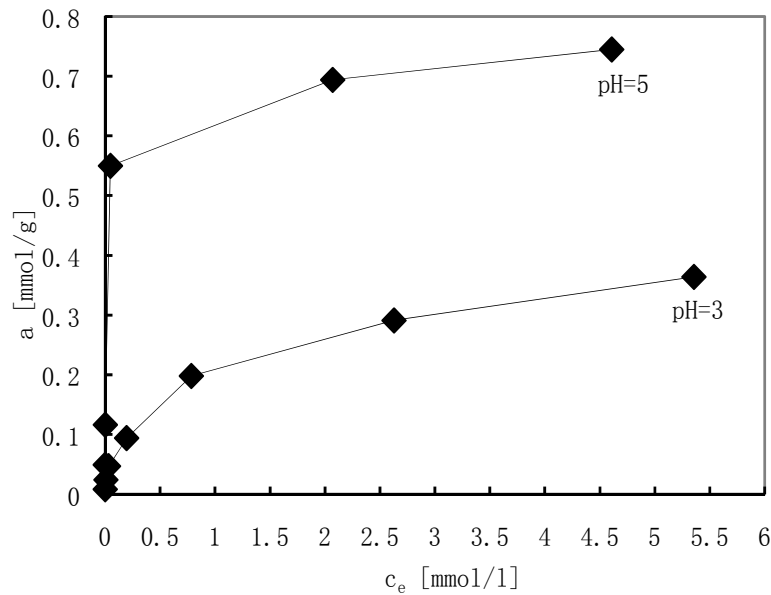


Fig. 1: Adsorption of lead on sample OA, pH= 3 and pH=5.

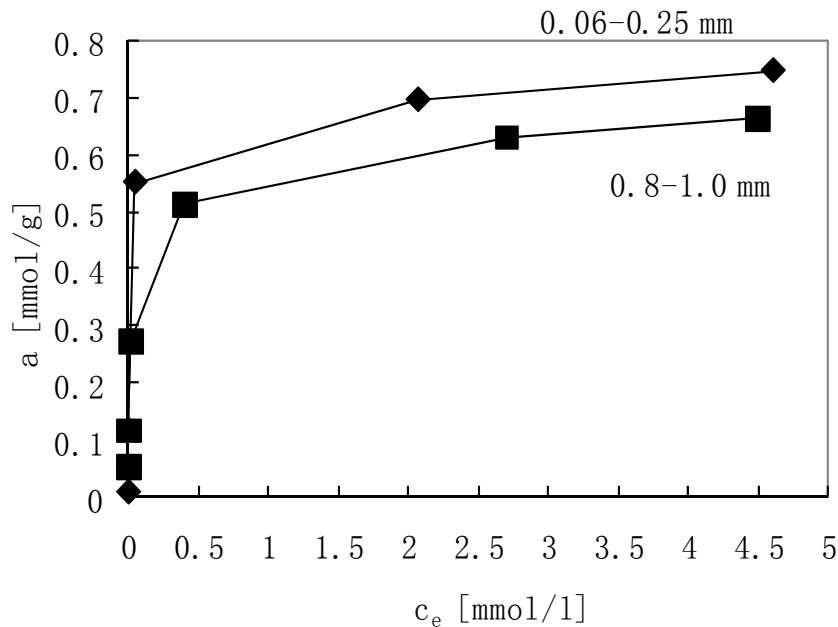


Fig. 2: Adsorption of lead on sample OA, diameters 0.06-0.25 and 0.8-1.0 mm

This figure indicates that the adsorption data could be well fitted by the Langmuir adsorption model (r -square values close to 1). In a linear form, the Langmuir equation is given by

$$c_e/a = c_e/a_m + 1/(a_m \cdot K) \quad (1)$$

Where a is the amount of the metallic ion adsorbed, c_e is an equilibrium concentration of the metallic ion in solution, K represents the monolayer binding constant and a_m is the monolayer adsorption capacity. The parameters a_m and K computed from the experimental data using equation (1) along with a coefficient of determination r^2 and equation of Langmuir isotherms are compiled in Table 2 for all studied samples.

Finally, on the basis of the experimental data, it is possible to assess roles of specific (cation exchange) and non-specific (double layer induced) types of adsorptions in the immobilization mechanism. With this respect, the HOA and the AC samples could be considered as quite different, „boundary“ types of the adsorbents - the humic acid HOA as a sample with a typical cation exchange process of immobilization mechanism, and, on the other hand, the activated carbon AC proving exclusively double layer induced type of immobilization. Evidently higher amount of immobilized cations for the HOA (OA) sample then suggests that the specific surface area is not so important factor while content of the acid groups appears to dominate.

Table 2: RESULTS obtained from the Langmuir equation applied to the adsorption data

Ion	Sample (0.06-0.25mm)	pH	$a_m(\text{mmol/g})$	$K(\text{l/mmol})$	r^2
Pb^{2+}	HOA	3	0.53	4.2	0.994
	OA	3	0.37	2.2	0.982
		5	0.75	42	0.999
	TA	5	0.30	5.7	0.958
	AC	3	0.123	1.4	0.998
	BC	5	0.193	2.0	0.993

3.3. Column Studies

Initial concentration of the adsorbate was the only variable parameter. The initial concentration of lead were 0.1, 1.0, 10 mmol/l. The breakthrough curves obtain for these feed concentrations are presented in Fig. 3 and the breakthrough data is summarised in Table 3.

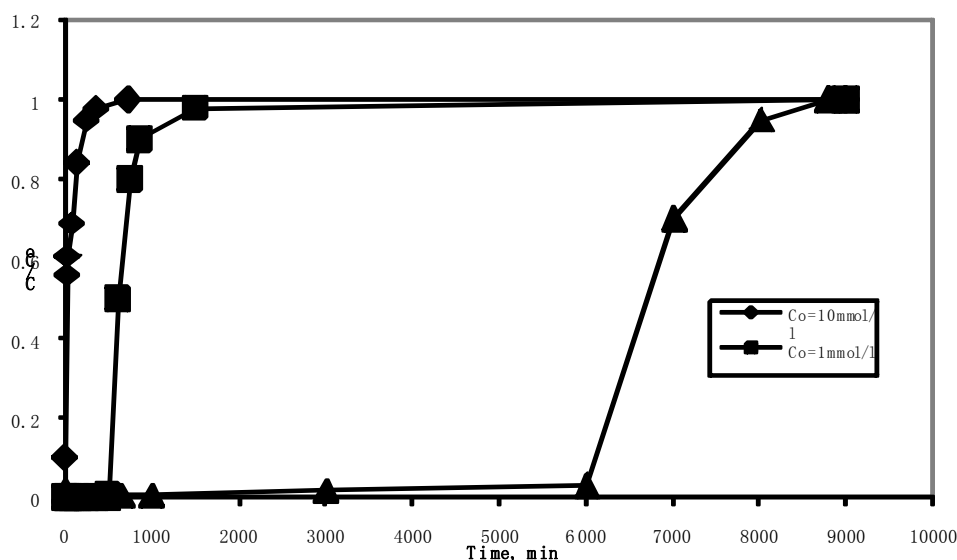


Fig. 3: Influence of concentration on breakthrough profile

The increase in initial concentration of the adsorbate leads to an early breakthrough and exhaustion of the bed. However, the adsorption at break point and exhaustion point does not change. Thus the adsorbent capacity is achieved earlier at higher adsorbate concentrations indicating that the fluid to adsorbent mass transfer rate of the solute increases. Similar results were published [7, 8].

Table 3. Effect of adsorbate concentration on breakthrough profile

Particle size	0.8 - 1.0 mm		Temperature	25°C		
Bed diameter	1.5 cm		Flow rate	1.4 ml/min		
Bed height	7.5 cm		Weight of the coal	10 g		
No.	C_o (mmol/l)	ρ_b (g/cm ³)	t_b (min)	t_e (min)	a (mmol/g)	a (mg/g)
1	10	0.75	≈ 5	≈ 300	0.09	18.65
2	1.0	0.75	≈ 400	≈ 1500	0.1	20.72
3	0.1	0.75	≈ 3000	≈ 8000	0.1	20.72

ρ_b – adsorbent bed density, t_b – breakthrough time (breakthrough concentration is taken as 5% of C_0), t_e – bed exhaustion time (bed exhaustion concentration is taken as 95% of C_0), a – amount adsorbed on adsorbent.

Amount adsorbed on OA is about three times lower than in batch experiment but on other hand contact time is markedly shorter.

4. Conclusions

The present work has led to some important conclusions as states below:

- The adsorption capacity of the adsorbent increases with the increase of pH.
- Particle size is important factor but there are not big differences of adsorption capacities between 0.06-0.25 mm and 0.8 – 1.0 mm.
- Langmuir adsorption isotherm good fit for adsorption of lead on coal.
- Specific adsorption on oxidative altered coal plays key role at immobilization of lead from solution
- In spite of lower adsorption capacity dynamic adsorption can be used for removal Pb^{2+} from wastewater.

5. Acknowledgements

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