Research Article

Lignitic Humic Acids as Environmentally-Friendly Adsorbent for Heavy Metals

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Received 15 December 2016; Accepted 22 January 2017; Published 5 March 2017

Academic Editor: Ziya A. Khan

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Humic acids are a part of humus material, are abundant in nature, and form a substantial pool of natural organic matter. They participate in the transport of both beneficial and harmful species. Due to their structure and properties, they can interact with metal ions and, with them, form relatively stable complexes. These substances are thus responsible for the so-called self-cleaning ability of soils. Lignite as a young coal type contains a relatively high amount of humic acids which can be used as an environmentally-friendly adsorbent for heavy metals. In this work, we compared the adsorption of single Cu^{2+} ions with the simultaneous adsorption of several different metal ions (Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+}). The adsorption efficiency of humic acids was very high, almost 100% in the case of the single adsorption of Cu^{2+} ions and more than 90% for the adsorption from the mixture of metal ions. The stability of formed complexes, considered on the basis of the leaching in different extraction agents, was higher than 80%; only 9–18% was in the mobile phase. After adsorption, metal ions are contained in humic acids after adsorption in mainly strongly bonded form (60–73%) and can be liberated from their structure only in low amounts.

1. Introduction

One of the most characteristic properties of humic substances is their adsorption ability [1–4]. They can bind to heavy metal ions, which are characterized by high toxicity and the ability to accumulate in the environment, and in this way, they can influence the effectiveness of regeneration and purification processes in soil and aqueous systems. Hence, the immobilization or removal of toxic metals is a research goal as well as an industrial task [5–7]. A cost-effective and environmentally-friendly approach is the use of sorption technology based on the use of sorbents prepared from some biomaterial [8, 9]. A potential low-cost sorbent of toxic metals and radionuclides for use in water treatment and ground-water remediation is lignite [2, 9–11]. When humic acids, as the most active constituents, were isolated from lignite and used as an adsorbent for metal ions, their effectivity and sorption capacity substantially increased [2]. In comparison with humic acids isolated from various soil types, lignitic humic acids exhibit a very high sorption capacity and a

low degree of desorption [6, 12]. On the other hand, humic acids isolated from oxyhumolite exhibited a lower sorption capacity in comparison with humic soil-derived humic acids [13]. The removal of heavy metals from aqueous systems such as waste streams employs various technologies which are often either expensive or inefficient, especially when very low residual concentrations compliant with health-based limits are required [7, 8]. On the basis of previous results, lignitic humic acids were used in this work for the environmentally-friendly adsorption of metal ions.

Interactions between humic acids and metal ions have a complex nature given by their heterogeneous, polyelectrolyte, and polydisperse character. Metal ions can bond with humic acids in several different ways from the purely electrostatic, nonspecific interaction of metal cation with the net negative charge on the surface of a humic particle to specific interactions in the formation of complexes and chelates with functional groups [1, 2, 4, 7, 14–16]. Due to the heterogeneous character of humic acids and their partial solubility in water, they can form water-soluble and water

TABLE 1: Elemental analysis of lignitic humic acids (normalized on dry ash-free sample).

C	H	N	S	O
42.7% at.	41.8% at.	0.9% at.	0.3% at.	14.3% at.

insoluble complexes with metal ions and other pollutants [4, 17–21]. Humic acids of low molecular weight had a much higher sorption capacity than those of high molecular weight or unfractionated humic material [13]. It was found that the binding of metals to humic acids depends on their type. The sorption capacity of humic acids for some metals is much higher than their possibilities given by the content of functional groups [4, 16]. Metal ions are bound to humic acids by different strengths and particular metals can exist in humic material in several different fractions [4, 22–26].

This work follows our previous adsorption studies [2, 4, 6] and is focused mainly on potential industrial applications such as the removal of heavy metals from waters, with an emphasis on the (often problematic) issue of low concentrations and the stability of the formed complexes.

2. Materials and Methods

Humic acids (HA) were extracted from South-Moravia lignite using a mixture of NaOH and $\text{Na}_4\text{P}_2\text{O}_7$ by means of a procedure described in our previous studies [4, 6] and characterized previously [4, 6, 27, 28]. Elemental analysis was carried out using a CHNSO Microanalyser Flash 1112 (Carlo Erba). The obtained values are listed in Table 1.

Humic acids and metal ion solutions (CdCl_2 , CuCl_2 , PbCl_2 , and ZnCl_2 , Sigma-Aldrich) were mixed in the ratio 1 g/50 mL and stirred to equilibrium (24 h). Then, solid humic particles were sequestered by centrifugation and the supernatant was analyzed. The quantity of the adsorbed amount was determined on the basis of the decrease in the metal ion concentration in the solution during sorption.

The stability of the formed complexes was studied using the extraction of metal ions by different agents. Water was used for the extraction of the mobile fraction (free unbound metal ions). A 1 M MgCl_2 solution was used as the extraction agent for the ion-exchangeable fraction (weakly bound metal ions). The strongly bound fraction of metal ions was extracted by a 1 M HCl solution. The extraction agents were chosen on the basis of results published in previous works [12, 29, 30].

The concentrations of metal ions in different solutions were measured by electrode coulometric titration (EcaFlow 150 GLP), based on the direct electrochemical conversion of the analyte species in the pores of the electrode or in a thin layer [17]. 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 and the stripping chronopotentiogram was recorded and evaluated.

All experiments were made in triplicate at 25°C (in an air-conditioned laboratory). The data are presented as average values with standard deviation.

TABLE 2: Average adsorption efficiencies for single Cu^{2+} ions and Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions adsorbed from their mixture.

Cu^{2+} (single)	Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
99.9%	90.3%	94.4%	92.8%	92.0%

TABLE 3: Average participation in total adsorption amount for Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions adsorbed from their mixture.

Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
21.0%	23.7%	31.7%	23.6%

3. Results and Discussion

In this work, the adsorption from low concentration metal ion solutions by solid humic acids was studied. We compared the adsorption of single Cu^{2+} ions with simultaneous adsorption of several different metal ions (Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+}). This concentration region was chosen on the basis of the potential utilization of humic substances as a low-cost sorbent for environmentally-friendly adsorption of toxic metal ions often occurring in low but still problematic and harmful concentrations. As we can see, the efficiency of adsorption in the case of single Cu^{2+} ions was almost 100% in the used concentration range. Its value slightly decreased with respect to adsorption from the mixture of metal ions, but the average efficiency was higher than 90% for all metal ions used (see Table 2).

The real efficiency fluctuated by 80 and 100% with the initial concentrations of metal ions (see Figure 1). Their values were thus very high over the whole concentration range and no specific trend was observed.

Comparing the percentages of metal ions that were adsorbed we can see that the most readily adsorbed metal was lead. Copper and zinc were adsorbed to a similar extent. Cadmium exhibited the lowest percentage, but its adsorption was only little worse than in the case of copper and zinc (see Table 3).

Since, the efficiency of adsorption was in many cases 100% and the used concentrations were low, it was not possible to fit experimental data by any of the usually used adsorption isotherms. We determined the “distribution coefficient” as the slope obtained from the dependence of adsorbed amount on equilibrium concentration, where data with efficiency lower than 100% were used (zero equilibrium concentrations for 100% adsorption efficiency were not included in the calculation). The highest values were obtained for the single adsorption of Cu^{2+} ions; in the case of adsorption from the mixture, this metal also had the highest distribution coefficient. Strong adsorption was also found for Pb^{2+} . On the other hand, the adsorption of Zn^{2+} was, according to the “distribution coefficient,” relatively weak. The obtained values of the “distribution coefficient” are not fully in agreement with the results listed in Tables 2 and 3. The reason is the above-mentioned partial elimination of some adsorption data because of the zero equilibrium concentration. Therefore, these values can be considered only as complementary

FIGURE 1: Amounts of metal ions adsorbed in dependence on their initial concentration in the mixture.

TABLE 4: Distribution coefficient for single Cu^{2+} ions and Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions adsorbed from their mixture.

Cu^{2+} (single)	Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
0.902 L/g	0.236 L/g	0.627 L/g	0.423 L/g	0.135 L/g

TABLE 5: Average contents of mobile phase, ion-exchangeable phase, strongly bound phase, and residual phase of single Cu^{2+} ions and Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions adsorbed from their mixture.

	Cu^{2+} (single)	Cd^{2+}	Cu^{2+}	Pb^{2+}	Zn^{2+}
Mobile phase	9.8%	14.4%	11.2%	12.4%	17.8%
Ion-exchangeable phase	17.0%	25.7%	18.0%	19.3%	21.8%
Strongly bound phase	22.2%	29.2%	23.6%	23.1%	26.7%
Residual phase	51.0%	30.7%	47.2%	45.2%	33.7%

ones for the complex illustration of the studied adsorption (see Table 4).

Although the average proportions of copper and zinc in the total adsorption amount were practically the same, their distributions according to bond strength were different. As we can see in Table 5, zinc was bound less strongly and larger part was present in mobile or ion-exchangeable form. Cadmium exhibited a similar content in the weakly bound mobile or ion-exchangeable form. On the other hand, copper and lead were bound strongly and only a small amount of these metals could be leached, for example, to water in nature. As can be seen, the individual extraction agents were able to leach different amounts of metal ions, which correspond with

different affinities of humic acids to the metal. Water is a weak leaching agent, which can extract only mobile fractions of metal ions. In order to obtain the ion-exchangeable fraction of metal ions a 1 M MgCl_2 solution was used. Metal ions extractable by a 1 M HCl solution constitute the fraction of strongly bound metal ions [12, 22, 29, 30]. Garcia-Mina [31] showed that the solubility of metal-humic complexes decreased with an increase in the metal : humic ratio, which could be related to the gradual reduction of the free ionized functional group in line with this increase. Our results confirmed this trend only partially, probably because of the use of low concentrations of metal ions. The strongly bound and residual phases were highest for copper and lead. These two metals were in large part strongly complexed in the humic structure and only a very small amount could be washed under normal conditions, as also confirmed by Dević [32]. Dudare and Klavins [33] showed that the complex stability constants significantly changed and were well correlated with the age and humification degree of humic acids. The lignitic humic acids used in our work belonged to the group of well-humified, more aromatic ones with a relatively high content of acidic functional groups, which predestines them for having a high complexation capacity for forming stable metal-humic complexes [7, 12, 34].

Our results correspond with some other works. Janoš et al. [23, 24] stated that Cu^{2+} and Pb^{2+} ions were bound very strongly to the sorbent and that only small portions of these metals could be extracted by weak agents. Substantial proportions of Cu^{2+} and Pb^{2+} ions remained in the residual fraction or were liberated only after the destruction of the organic matrix. On the other hand, Cd^{2+} and Zn^{2+} ions were retained less strongly in the sorbent, probably by an ion-exchange mechanism, and could be leached from the

sorbent in acid media. Town and Van Leeuwen [26] obtained similar results for the adsorption of Cd^{2+} , Cu^{2+} , and Pb^{2+} ions. Bosire et al. [35] showed that Zn^{2+} and Cu^{2+} ions were statistically different in their adsorption capacities. Their surface complexation models showed stronger lead and copper interactions with monodentate sites compared to bidentate sites. According to their results, the ratio of Pb^{2+} ions adsorbed on monodentate carboxylic acid sites to Pb^{2+} ions adsorbed on bidentate sites was approximately 1:1. A similar trend was observed for Cu^{2+} ions. The participation of monodentate sites increased with temperature and phenolic sites were involved in bonding only weakly. Yang and Van Den Berg [36] and Kostić et al. [37] confirmed that humic complexes formed with copper exhibited greater stability than those formed with zinc. The stability constant for the complex between lead and humic acids was greater than those for other metal-humic complexes. Terbouche et al. [38] showed that the degree of association between metal ions and humic acids was greater for zinc than for cadmium, which corresponds with our results. Ren et al. [39] divided Cd^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} ions occurring in contaminated soils into two groups: a fast exchangeable pool and a much slower exchangeable one. The distribution of the two exchangeable pools varied significantly among metals. The amount of cadmium related to the fast pool was dominant which could correspond with the highest amount of weakly bound Cd^{2+} ions found in this work. The authors stated that the exchange of cadmium was a relatively fast process, whereas the exchange of copper, lead, and zinc was more sluggish, which is of significant importance for the metal mobility, risk assessment, and management of contaminated soils.

Our results showed that the partitioning of metal ions according to bond strength depends on the presence of other metal ions. The strongly bound and residual fractions decreased in the case of adsorption from the mixture of metal ions, probably due to occupation of strong binding sites by other ions. This was connected with the decrease in adsorption efficiency when compared with the single adsorption of Cu^{2+} ions. On the other hand, the efficiency was, in all cases, higher than 80% and in some cases it achieved 100%. This is a very good result with respect to the potential application of lignitic humic acids as an environmentally-friendly adsorbent for heavy metals. It was found that the leaching of metal ions from humic acids into water was very low; in most of cases it was about 10% and did not exceed 20%. The majority of metal ions ($\geq 60\%$) were bound very strongly and only partially leachable under strongly acidic conditions.

4. Conclusions

Humic acids isolated from lignite were investigated in order to evaluate their use as an environmentally-friendly adsorbent of heavy metals. Lignite, as a young coal type, contains a relatively high amount of humic acids and can be used for the low-cost production of these valuable substances. It was found that their adsorption efficiency is very high, usually between 80 and 100%. The stability of the formed complexes was evaluated on the basis of leaching using different extraction agents. Copper and lead were bound very

strongly in metal ion-humic complexes and their leaching was low. On the other hand, the amount of cadmium and zinc in the mobile and ion-exchangeable phases was higher (in comparison with copper) but this amount did not exceed 40% of the total content of cadmium and zinc in humic acids. It was confirmed that lignitic humic acids are suitable adsorbent for heavy metals and can be used also for cleaning of waters, soils, and other systems with low or residual concentrations of metal ions. Their partial binding in the mobile and ion-exchangeable phases can be compensated for or eliminated by the use of fresh humic acids without the possibility of the backward leaching of metal ions into the cleaned system.

Competing Interests

The authors declare no conflict of interests regarding the publication of this paper.

Authors' Contributions

Marcela Pavlíková and Martina Klučáková performed the experiments; Marcela Pavlíková and Martina Klučáková analyzed the data; Martina Klučáková wrote the paper.

Acknowledgments

This research was supported by Materials Research Centre at FCH BUT-Sustainability and Development, REG LO1211, with financial support from National Programme for Sustainability I (Ministry of Education, Youth and Sports).

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