Sustainable Environment Research 26 (2016) 136–141

Contents lists available at ScienceDirect

Sustainable Environment Research

journal homepage: www.journals.elsevier.com/sustainable-environment-research/

Original research article

Adsorption study of mercury on lignite in the presence of different anions

Irma Robles [a], [b], Erika Bustos [a], János Lakatos [b], *

[a] Center of Research and Technological Development in Electrochemistry, Pedro Escobedo 76703, Mexico
[b] Institute of Chemistry, University of Miskolc, Miskolc-Egyetemváros 3515, Hungary

ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form
6 December 2015
Accepted 19 January 2016
Available online 12 April 2016

Keywords:
Mercury
Inorganic
Biomass
Coal
Activated carbon

ABSTRACT

This study compares the effect of different anions such as chloride, nitrate, and sulphate on the mercury adsorption onto lignite, which was a model material for the humus-containing organics in soil, and can be considered as a natural sorbent in the remediation of contaminated sites. Since the complex formation can significantly influence the mercury sorption, besides chloride, the effects of other complex-forming agents such as ethylenediaminetetraacetic acid, and thiocyanate were also tested. Various batch type and dynamic experiments were performed and four sorption models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were used to evaluate the sorption data.

1. Introduction

Mercury is one of the most toxic heavy metals to living organisms and humans [1–5]. Soil can absorb significant amounts of mercury that is distributed between its solid, liquid and gas phases and, specifically in the solid phase, mercury can be adsorbed onto different components of the organic matter and minerals [6]. It is well known that the high sorption capacity of the upper layer of soil protects the deeper soil region from contamination and restricts the mercury transport toward the underground water source. Depending on the type of soil, the clay and humus content will be the principal components responsible for the mercury retention. The origin of surface organics is due to vegetation, therefore a stabilized non-living biomass formation such as lignite was used as a model compound instead of organic soil materials.

Specifically, lignite is an organic substance present in the early stages of coalification [7–11]. It has natural ion exchange properties because of the presence of carboxylic, phenolic functional groups attached to a highly cross-linked structure of aromatic compounds as seen in Fig. 1 (adapted from Ref. [12]). The natural ion exchange property of lignite depends on the number of sorption sites or functionalities. Since lignite is a low-grade coal and has a high oxygen content, it is expected that it would have a high sorption capacity [13]. The carboxyl functional groups existing on the surface of the solid are the most important sites involved in the ion-exchange process. The carboxyl groups occur as metal carboxylates and the metal ion is readily exchanged with cations that have a higher affinity for the coal surface. Natural cation exchange capacity of lignite can reach 0.5 meq g^{-1}.

The adsorption of metal ions on exchange sites of coal has been attributed to reactions as illustrated by Eq. (1), where M denotes a metal ion of charge n, M_1 can mean that the cation (Ca^{2+}, Mg^{2+}, Na^+, K^+, Fe^{3+}, etc.) is the exchange site on the natural lignite, and M_2 represents the sorbed ion [13–16]:

$$coal-\left(COO^{-}\right)_n M_1^{n+} + M_2^{n+} \leftrightarrow coal-\left(COO^{-}\right)_n M_2^{n+} + M_1^{n+} \qquad (1)$$

Besides the ion exchange, when the metal ion occupies a few ligand positions on the sorbent surface, different complexes (often chelates) can be formed. The order of decreasing affinity of organic functionalities (ligands) for metal ion bindings is approximately as follows: $-O- > -NH_2 > -N{=}N- > {=}N > -COO^- > -O^- > C{=}O$, while the stability of metal-humic complexes follows the Irving–Williams series: $Hg > Cu > Ni = Zn > Co > Mn = Cd > Ca > Mg$ [17–22]. The complexing ability of humic and fulvic acids is due to the large amounts of oxygen-containing functional groups, such

---

* Corresponding author.
E-mail address: mtasotak@uni-miskolc.hu (J. Lakatos).
Peer review under responsibility of Chinese Institute of Environmental Engineering.

http://dx.doi.org/10.1016/j.serj.2016.04.008

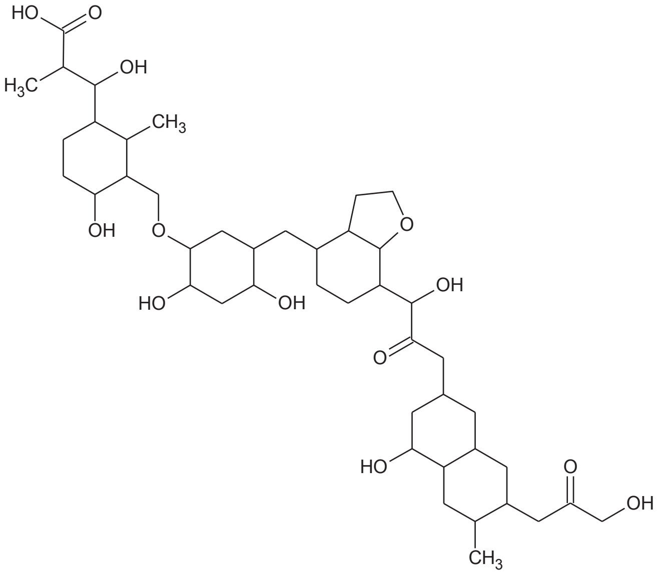

Fig. 1. Structural unit of lignite model (adapted from Ref. [12]).

as the −COOH, phenolic −OH and −C=O groups that exist on the surface of these materials. Low-molecular-weight compounds, such as fulvic acids, bring about the solubilisation of metal ions and affect their transport to plant roots. In contrast, high-molecular-weight compounds (humic acids) can be considered as a “sink” for polyvalent cations. Natural complexing agents are of considerable importance in weathering processes [23–26].

Mercury may be present in soil in three different oxidation states, where the most reduced one is the metallic form of mercury (Hg^0). The other forms are ionic, mercurous ion ($Hg_2{}^{2+}$) and mercuric ion (Hg^{2+}). The mercurous ion is not stable since it dismutates into Hg^0 and Hg^{2+}. Pourbaix diagrams for mercury reported by Schuster and Allard indicate that the existence of the forms of inorganic mercury species depends on the function of pH and redox potential [7,27].

Since Hg(II) has a high affinity for forming ion associations and complex ion formations, the present study was carried out to elucidate adsorption parameters that influence the mercury adsorption onto lignite using different counter-ions such as chloride, nitrate and sulphate. These results were also compared with the uptake of copper. Some extracting agents were also used to analyze how they affect mercury adsorption. The time and pH dependence of Hg(II) adsorption were analyzed and theoretical isotherm models were used to fit adsorption results. Various batch type and dynamic experiments were performed and four sorption models (Langmuir, Freundlich, Temkin and Dubinin-Radushkevich) were used to evaluate the sorption data.

2. Materials and methods

The lignite used in the investigation originated from an open pit mine from Bükkábrány, Hungary. A few data characteristics of the lignite, which was produced in three size fractions, are shown in Table 1.

The counter-ions used in this study were chloride, nitrate and sulphate. A stock solution of mercury and copper in distilled water was prepared using mercury chloride ($HgCl_2$) and copper chloride ($CuCl_2 \cdot 2H_2O$) both obtained from Reanal (Hungary) and monohydrate mercury nitrate ($Hg(NO_3)_2 \cdot H_2O$) and mercury sulphate ($HgSO_4$), both obtained from ACS Merck (Germany). In the study of the effect of the complexing agent ethylenediaminetetraacetic acid (EDTA), potassium-thiocyanate (KSCN) and sodium chloride were used; all of them obtained from Reanal. All the substances used were reagent grade. In addition to mercury, copper was used in the sorption study for comparison.

Table 1
Composition data of different size fractions of Bükkábrány lignite.

Parameter (w/w %)	Lignite (Bükkábrány) $0.063 < d < 0.25$ mm	Lignite (Bükkábrány) $0.25 < d < 0.5$ mm	Lignite (Bükkábrány) $0.5 < d < 1$ mm
Humidity	6.5	7.0	7.0
Ash	19.5	20.7	15.9
C	50.8		
H	5.0		
N	0.9		
S	2.7		

In the case of the investigation of time dependence of adsorption, 5 mM solutions of Cu(II) and Hg(II) were prepared in distilled water. In the sorption tests, the solid−liquid ratio was 1:50 (g:mL). The batch type of tests was static, meaning the slurries were shaken only once a day. The pH effect in the case of Hg(II) was studied using a solution of $HgCl_2$, $Hg(NO_3)_2$ and $HgSO_4$. The pH was set between 1 and 7 by the corresponding acids (hydrochloric-, nitric- and sulphuric-acids). In the tests, different mercury compounds such as $Hg(NO_3)_2$, $HgSO_4$ and $HgCl_2$ at a 1 mM concentration were used.

Some dynamic experiments were done in order to compare copper and mercury uptake on lignite because they have the same oxidation number. The schematic of the dynamic test is shown in Fig. 2.

The effect of different complexing agents (e.g., chloride, thiocyanate and EDTA) was also investigated. Since the sorption in the previous investigations was found to be a time-dependent process, sorption as a function of time was also tested.

Mercury and copper concentrations were measured using a Flame Atomic Absorption Spectrophotometer (PU 9100 Philips, Amsterdam). All experiments were carried out at room temperature.

3. Results and discussion

3.1. Sorbent characterization by Cu loading

Since, according to the literature, mercury sorption on organic substances is expected to be a complex process, the sorption and reduction of the sorbent was pretested for characterization purposes by a non-reducing element such as Cu(II) ion. The sorption isotherms were determined for each of the size fractions of lignite using a static batch type experiment and 5 d of contact time. The

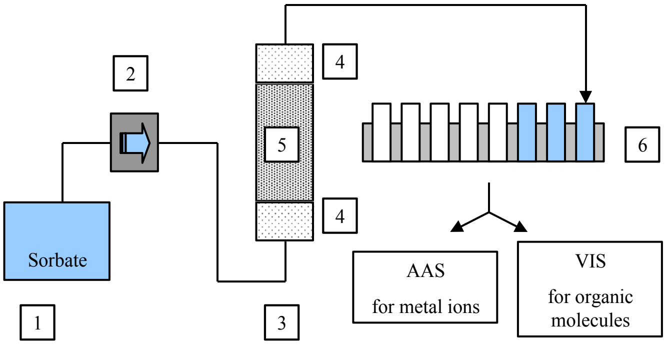

Fig. 2. Schematic of dynamic experiment of sorption (1: Sorbate solution container, 2: Peristaltic pump, 3: Sorption column, 4: Sand filter bed, 5: Sorbent + sand mixture bed, 6: Fraction collector).