Adsorption of Cu(II) from aqueous solution using raw peat: preliminary results

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Abstract. Peat is a polar, highly porous material that could have significant applications as an adsorbent for removal of heavy metals from aqueous solutions. Various functional groups in lignin allow such compounds to bind on active sites of peat. The adsorption of Cu (II) from aqueous solutions on peat from the West Siberia was studied in the concentration range of 10–150 mg/L and time variations of 0.25-12 hours. The pH of the solutions varied over a range of 3.2–4.3. The adsorption data could be fitted to a Freundlich adsorption isotherm and the maximum adsorption capacity of peat was determined to be $2.5 \cdot 10^{-3}$ mmol/g when the initial concentration for Cu^{2+} was at its minimum (0.05 mmol/L), and the time of adsorption was 30 minutes.

1 Introduction

In recent decades, sorption methods have found application in the technology of extraction and concentration of metals from aqueous solutions. However, most of the sorbents offered for practical use are inaccessible. In this connection, the search and investigation of inexpensive sorbents possessing high sorption capacity and selectivity with respect to heavy metals is relevant. Biosorbents are of particular interest. Peat has been widely used as a low cost adsorbent to remove a variety of materials including organic compounds and heavy metals from water [1, 2].

In recent years, there has been a rapid growth of research concerning the use of biomaterials both in the native state and in the form of modified products for the removal of heavy metal ions from aqueous media [3, 4]. The sorption properties of peat are determined by the developed porous structure and the presence of a large variety of functional groups having physical and chemical adsorption. The most active constituent of peats are humic acids (HA), which participate in the reactions of ion exchange, complexation, and sorption interactions. The humic substances contained in peat form strong compounds with heavy metals and can be used as a powerful geochemical barrier [5-8].

Researchers have proposed various mechanisms of metal ion binding to peat including ion exchange, complexation, and surface adsorption. The objectives of this work were to characterize the Siberian peat in terms of its adsorption characteristics for Cu^{2+} under different concentrations and time variations.

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2 Experiment and methods of analyzes

West Siberian peat from forest steppe was used as adsorbent in this study. The dried and sieved peat (<250 µm), 0.5 g, was diluted with 50 ml of the prepared solution with $Cu(NO_3)_2$ contents of 10, 25, 50, 100, and 150 mg/L. Then the flasks were placed on a magnetic stirrer for a different period of time (15 min, 30 min, 2, 4, 8, 12 hours). After the experiment, the pH, ORP, conductivity, and temperature were immediately measured. The samples were then centrifuged and filtered through a membrane filter (0.45 µm).

The water samples before and after interaction with sorbents were analyzed by ICP-MS and ICP-AES method using ELEMENT spectrometer (Finnigan MAT) in the Institute of Geology and Mineralogy SB RAS. The solid samples before and after experiments were dried at room temperature, homogenized, and analysed by X-ray fluorescence with synchrotron radiation (XRF SR) at the VEPP-3 station in the Institute of the Nuclear Physics SB RAS. The element and mineral composition of the solid samples were analysed after the experiments using the scanning electron microscope (SEM) Jeol JSM-638OLA.

3 Results and discussion

3.1 Experiments

The results are given in terms of removal percent (%*R*) and distribution ratio, *K*d (ml/g) which were calculated on the equations:

$$\%R = 100(Co - Ce)/Co, \quad (1)$$

and

$$Kd = [(Co - Ce)/Ce]\ [V/M] \quad (2)$$

where *C*o = initial concentration of copper in solution (mmol/L); *C*e = concentration of cooper in solution after equilibration (mmol/L); *V* = volume of solution (ml), and *M* = mass of peat (g). The degree of Cu^{2+} ion extraction on the studied sorbents depends on its initial concentration in solution (*C*o) (Fig.1).

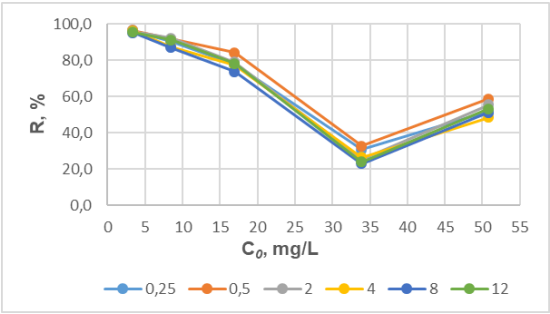

Fig. 1. Change in the degree of Cu^{2+} ion extraction vs. its initial concentration on natural sorbent at various interaction times of solutions with sorbent.

With increasing in initial concentration of copper, the extraction degree of Cu^{2+} ions on peat decreases due to a reduction in adsorption sites. The degree of extraction increases with increasing in the concentration of adsorbed ions to 33 mg/L, that is likely due to partial desorption of Cu^{2+} ions.

Distribution ratio (Fig. 2) shows sorption is most efficient at the lowest Cu concentration in solution. Sorption runs quickly, in the first 30 min. At low concentrations, Cu^{2+} ions have relatively high chemical affinity with sorbent surface. The number of vacant adsorption sites decreases with filling of sorption points, and the adsorbed substance consequently reduces. pH values demonstrate directly proportional dependence: distribution ratio increases with increasing in pH, however the lower concentrations have pH from 3.6 to 4.2, and higher concentration solutions have the lowest pH of 3.2-3.6. Regular changes of copper in solution indicate a predominance of sorption affecting the visible change in the solution pH.

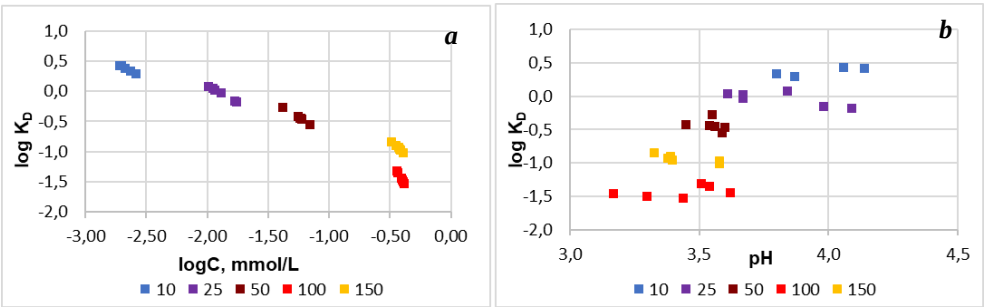

Fig. 2. Distribution ratio Kd vs. copper concentration in solution (a) and pH (b).

3.2 Equilibrium adsorption isotherms of copper on peat

For a quantitative description of the sorption equilibrium in the range of given concentrations, the Langmuir and Freundlich models were used [9, 10]. Fig. 3 shows the graph obtained for the adsorption isotherm of Cu (II) onto the peat under investigation. This graph indicates an *L*-type adsorption isotherm, which is characterized by a decreasing slope as the adsorbate concentration increases due to increased coverage of vacant adsorption sites [11]. These results were then analyzed by using a Langmuir, and a Freundlich sorption isotherms.

The Langmuir equation is theoretically derived from simple mass-action kinetics, assuming chemisorption. The following well-known linearized form of the Langmuir equation has been used to analyze the obtained adsorption results:

$$Ce/qe = 1/KLQ + Ce/Q \tag{3}$$

where *Ce* and *qe* have the same definitions mentioned before; *Q* is the adsorption maximum or what is generally termed the monolayer capacity and has the units of *qe* (mmol/g); and *K*L is a constant related to the intensity of adsorption (l/kg of peat).

As shown in Fig. 4 (*a*), the plot of *Ce/qe vs. Ce* is a straight line indicating conformity of the adsorption data with the Langmuir equation over the initial cooper concentration range in between 0.05 and 0.8 mmol/L. From the slope and intercept of the straight line, the values of *Q* and *K*L were estimated and are listed in Table 1. The correlation factor is also listed in the table showing that the linear fit of *Ce/qe vs.Ce* is not so good. The validity of the Langmuir equation over the specified concentration range (0.05–0.8 mmol/L) does not indicate monolayer coverage of the surface of peat moss by cooper.

Graphical solution of the linear Langmuir equation for sorption of Cu (II) ions on peat gives the following values $Q = 2.5 \cdot 10^{-3}$ mmol/g, and a constant = $0.76 \cdot 10^{2}$ (Table).

Unlike the Langmuir equation, the Freundlich isotherm is empirical and has been derived by assuming a heterogeneous surface with a nonuniform distribution of the heat of adsorption over the surface [12]. The linear expression of this isotherm can be written:

$$\log qe = \log K + (1/n) \log Ce \quad (4)$$

where qe is the amount of cooper adsorbed per gram of peat (mmol/g); Ce is the equilibrium concentration of cooper in solution (mmol/L); and K and $1/n$ are positivevalued adjustable parameters. The parameter $1/n$ is constrained to lie between zero and one and it is a measure of the heterogeneity of adsorption sites on the surface of the adsorbent. As illustrated in Fig. 4 (b), a plot of log qe *vs.* log Ce is a straight line indicating the validity of the Freundlich expression over the range of cooper concentration (0.05–0.8 mmol/L) studied. From the slope and the intercept of the straight line, the values of K and $1/n$ have been determined and are given, together with the correlation factor r^2, in the Table. The relatively low value of $1/n$ (0.2956) indicates a heterogeneous surface with an exponential distribution of energy of the adsorption sites, that is all surface sites are not identical.

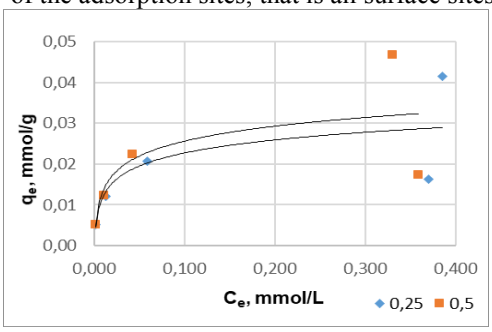

Fig. 3. Adsorption isotherm of Cu (II) onto peat for 15 and 30 min.

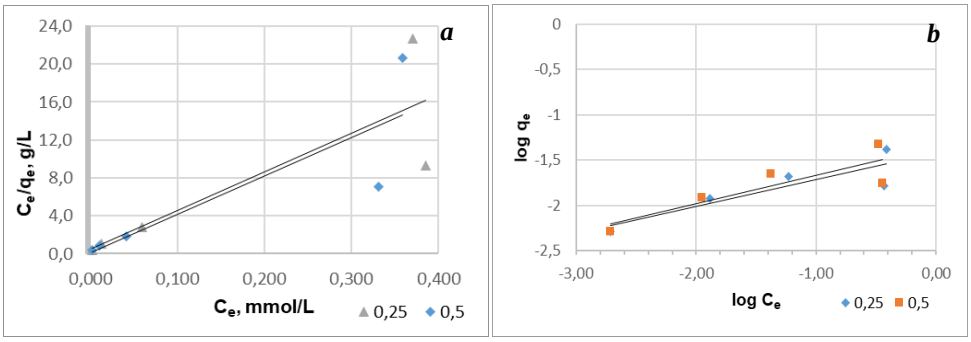

Fig. 4. Langmuir (a) and Freundlich (b) plots of Cu (II) sorption onto peat for 15 and 30 min.

Table. Isotherms parameters and correlation factors.

Isotherm	**Parameters and correlation factors**			
Langmuir	Q (μmol/g)	KLQ	KL	r^2
	0.025	7.3584	297.8	0.7324
Freundlich	1/n	n	k	r^2
	0.2956	3.38295	1.4176	0.7714

4 Conclusions

The studies showed that equilibrium of cooper adsorption is established in less than 30 minutes. Under optimized conditions, the removal performance was found to be efficient enough, reaching 96%. A slight increase in pH of the solution was observed following cooper adsorption. This could be interpreted by reverse hydrolysis reactions, which consume H^+, thus raising the pH. Freundlich, and Langmuir equations are followed and the corresponding constants were established. The loading capacity using Langmuir isotherm was found to be $Q = 2.5 \cdot 10^{-3}$ mmol/g and the constant $0.76 \cdot 10^2$ was evaluated. The process could be efficiently used for removal of cooper from low-level liquid waste. The obtained experimental data provide a prediction of similar sorption capacity of peats with congruent material composition in relation to Cu^{2+} ions.

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References

1. T. Leiviskä, M. K. Khalid, H. Gogoi, J. Tanskanen, Enhancing peat metal sorption and settling characteristics. Ecotoxicology and Environmental Safety, **148**, 346-351 (2018) doi:10.1016/j.ecoenv.2017.10.053
2. P. Bartczak, M. Norman, Ł. Klapiszewski, N. Karwańska, M. Kawalec, M. Baczyńska, T. Jesionowski, Removal of nickel(II) and lead(II) ions from aqueous solution using peat as a low-cost adsorbent: A kinetic and equilibrium study. Arabian Journal of Chemistry, **11**(8), 1209-1222 (2018) doi:10.1016/j.arabjc.2015.07.018B
3. C. F.Carolin, P.S. Kumar, A. Saravanan, G.J. Joshiba, M. Naushad, Efficient techniques for the removal of toxic heavy metals from aquatic environment: A review. Journal of Environmental Chemical Engineering, **5**(3), 2782-2799 (2017) doi:10.1016/j.jece.2017.05.029
4. N.B. Singh, G. Nagpal, S. Agrawal, Water purification by using adsorbents: A review. Environmental Technology and Innovation, **11**, 187-240 (2018) doi:10.1016/j.eti.2018.05.006
5. G. McKay, J.F. Porter, Equilibrium parameters for the sorption of copper, cadmium and zinc ions onto peat. Journal of Chemical Technology and Biotechnology, **69**, 309–320 (1997)
6. Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat. Water Research, **34**, 735–741 (1999)
7. A.P. Brown, S.A. Gill, S.J. Allen, Metal removal from wastewater using peat. Water Research, **34**, 3907-3916 (2000)
8. P. Villaverde, D. Gondar, J. Antelo, R. Lopez, S. Fiol, F. Arce, Influence of pH on copper, lead and cadmium binding by an ombrotrophic peat. Eur. J. Soil Sci., **60**, 377-385 (2009)
9. I. Langmuir, The Constitution and Fundamental Properties of Solids and Liquids J. Am. Chem. Soc., **38**, 2221 (1916)
10. H.M.F. Freundlich, Over the Adsorption in Solution J. Phys. Chem., A **57**, 385 (1906)
11. M.E. Essington, *Soil and Water Chemistry; an Investigative Approach* (CRC Press, London, 2000).
12. T.W. Brunauer, *The Adsorption of Gases and Vapors. Vol. 1* (In: Physical Adsorption. Princeton University Press, Princeton, 1943).