

Investigation of metal ions sorption of brown peat moss powder

Nadezhda Kelus, Elena Blokhina, Dmitry Novikov, Yaroslavna Novikova, and Vladimir Chuchalin

Citation: *AIP Conference Proceedings* **1899**, 050002 (2017); doi: 10.1063/1.5009865

View online: <https://doi.org/10.1063/1.5009865>

View Table of Contents: <http://aip.scitation.org/toc/apc/1899/1>

Published by the [American Institute of Physics](#)

Articles you may be interested in

[Adsorption properties of Silochrom chemically modified with nickel acetylacetonate](#)

AIP Conference Proceedings **1899**, 020006 (2017); 10.1063/1.5009831

[Computation of probabilities of transit of gas particles through channels with rough wall](#)

AIP Conference Proceedings **1899**, 060001 (2017); 10.1063/1.5009872

[Embryotoxicity of poorly soluble nanoparticles at various stages of Zebrafish development](#)

AIP Conference Proceedings **1899**, 050004 (2017); 10.1063/1.5009867

[Impact of heavy metals on photosynthetic pigment content in roadside plant communities](#)

AIP Conference Proceedings **1899**, 050003 (2017); 10.1063/1.5009866

[Synthesis of the boron-based coating in beam plasma using fore-vacuum electron source](#)

AIP Conference Proceedings **1899**, 040004 (2017); 10.1063/1.5009859

[Geotechnical consulting at the stages of design and full repair: A case study of village school in Minusinsk region, Russia](#)

AIP Conference Proceedings **1899**, 060019 (2017); 10.1063/1.5009890

AIP | Conference Proceedings

Get **30% off** all
print proceedings!

Enter Promotion Code **PDF30** at checkout



Investigation of Metal Ions Sorption of Brown Peat Moss Powder

Nadezhda Kelus^{1,a)}, Elena Blokhina^{2,b)}, Dmitry Novikov^{2,c)},
Yaroslavna Novikova^{1,d)}, Vladimir Chuchalin^{1,e)}

¹Siberian State Medical University, 2, Moscovski Trakt ave., Tomsk, 634050, Russian Federation

²National Research Tomsk State University, 36, Lenina ave., Tomsk, 634050, Russian Federation

^{a)}Corresponding author: knv07@mail.ru,

^{b)}lpina5940@rambler.ru

^{c)}novikov.tsu@gmail.com

^{d)}Novicova.yaroslavna@mail.ru

^{e)}phtech@ssmu.ru

Abstract. For regularities research of sorptive extraction of heavy metal ions by cellulose and its derivatives from aquatic solution of electrolytes it is necessary to find possible mechanism of sorption process and to choose a model describing this process. The present article investigates the regularities of divalent metals sorption on brown peat moss powder. The results show that sorption isotherm of Al^{3+} ions is described by Freundlich isotherm and sorption isotherms of Na^+ и Ni^{2+} are described by Langmuir isotherm. To identify the mechanisms of brown peat moss powder sorption the IR-spectra of the initial brown peat moss powder samples and brown peat moss powder samples after Ni (II) sorption were studied. Metal ion binding mechanisms by brown peat moss powder points to ion exchange, physical adsorption, and complex formation with hydroxyl and carboxyl groups.

INTRODUCTION

Sorption from solutions on polymeric materials is base of many physical-chemical processes related to bacteria's vital activity, technogenic activity, collection of different substances and utilization of by-products. For regularities research of sorptive extraction of heavy metal ions by cellulose and its derivatives from aquatic solution of electrolytes and for finding possible mechanism of sorption process (nature of sorptive center and nature of sorptive center and ion interaction) it is necessary to have an information about physico-chemical properties of polymeric sorbates based on cellulose, properties of water phase, also dates about influence of different conditions on adsorption equilibrium, such as metal and polymer nature, composition and pH of medium, temperature ect.

Theoretical and practical issues of metal ions sorption by plant materials based on cellulose were mentioned by many russian and foreign scientists – Nikitin N.I., Rogovin Z.A., Saldadze K.M., Kopylova-Valova V.D., Baiklz N., Segal L., Klemm D., Hubbe M.A. etc.

However, nowadays there is no the concurrent view of scientists regarding the mechanism of sorption of heavy metal ions from aqueous media by cellulose materials and the choice of a model for describing this process. Among the possible mechanisms of sorption are ionic replacement on the carboxyl ion, ionic replacement and complexing by the interaction with hydroxyl group, also complexing which involves all oxygen atoms of the elemental cellulose unit. For sorption isotherm processing the range of models is treated that exact describe the equilibrium in the heterophase system «aqueous solution of metal salt - sorbing agent containing cellulose. That all indicates the absence of a general approach to the description of the process of heavy metal ions sorption by plant material based on cellulose and guide for sorption model selection [1-5].

Nowadays heavy metals are classified among the top environmental contaminating agents. The accumulation of metals in a body can lead to serious diseases. Metals have a great effect on metabolism, as a rule, their impact on cells is non-specific. Sorption from solution is a basis for many physical and chemical processes connected with both functioning of microorganisms and technology-related activities. This fact determines the need to fix physical and chemical regularities of heavy metal sorption form water medium by brown peat moss powder [6].

Enterosorbents, which are able to remove toxic and pathogen agents from the body, are finding growing application in preventive care and treatment of animal and human diseases. Sphagnum moss or peat moss has been used in traditional medicine since the XI century. However, it has gained scientific recognition only at the present time after the study of their adsorption properties. Previously, in our experiments we showed that sphagnum moss possesses absorption and detoxification properties [7].

The purpose of this paper is to study the regularities of aliovalent metals sorption on brown peat moss powder.

EXPERIMENTAL PART

Materials and methods

The object of the study was turf sphagnum moss (*Sphagnum fuscum* (Schimp.)). *Sphagnum fuscum* was collected in the Chaginskoye marsh (Tomsk region, Russia). *Sphagnum fuscum* was dried out in the ventilated room to the air-dry state. The dried plant was crushed up to 0.1 mm. High-dispersive powder was obtained with the help of an analytical mill (IKA, Germany).

Using Agilent 4100 Microwave Plasma-Atomic Emission Spectrometer (Agilent Technologies, USA) we studied sorption activity of brown peat moss powder (BPMP) with 0.1mm particle size in relation to sodium ions (I), nickel ions (II), aluminium ions (III).

The method of determining sorption of sodium ions (I): 500 mg of BPMP was placed in a 50 cm³ flask and adjusted to the mark with sodium nitrate solution in the following concentrations: 0.00001, 0.00002, 0.0001, 0.001, 0.003, 0.005, 0.015, 0.02, 0.1, and 0.2 mol/l. The flasks were hermetically sealed and left for 2 hours at room temperature (23±2°C). Then the suspension was filtered through the filter paper under pressure.

Sodium percentage was determined in work standard solutions (WSS) and solutions after BPMP sorption. The concentration of sorbed sodium in grams per one gram of the sample was determined using the formula:

$$X = (C_{WSS} - C_{TS}) \cdot 1000 \quad (1)$$

where, C_{WSS} is sodium concentration (mg/g) in the solutions before sorption and C_{TS} is sodium concentration (mg/g) in the test solution after sorption.

Sodium concentration was determined at the wavelength of 588.995 nm. Previously the calibration curve had been constructed. To construct the calibration curve in the range of 1.0 - 4 mg/l 3 calibration solutions were prepared. Using analytical scales we weighed 52 mcl; 104 mcl; 126.3 mcl of the standard sample (State Standard Sample 7474-98 sodium ions 1mg/sm³), then placed in a flask and adjusted to the mark with purified water. Afterwards the concentration of sodium ions in calibration solution was determined using the formula:

$$X_{cs} = \frac{C_{WSS} \cdot m_{sw}}{V} \quad (2)$$

where X_{cs} is the concentration of sodium ions in calibration solution, mg/l;

C_{WSS} is the concentration of sodium ions in work standard solution, mg/l;

m_{sw} is the sample weight, mg;

V is flask volume, ml

Method of determining the sorption of nickel ions (II): 200 mg of BPMP (0.1 mm particle size) was placed in a 50 ml flask and adjusted to the mark with nickel nitrate 6-aqueous solution in the following concentrations: 0.0001, 0.00002, 0.005, 0.02, 0.1, 0.2, 0.04, 0.6, 0.8, and 1.0 mol/l.

The flasks were hermetically sealed and left for 24 hours at room temperature (18±2°C). Then the suspension was filtered through the filter paper under pressure.

The concentration of sorbed nickel in grams per one gram of the sample was determined using the formula:

$$X = (C_{WSS} - C_{TS}) \cdot 1000 \quad (3)$$

where, C_{WSS} is nickel concentration (mg/g) in the solutions before sorption and C_{TS} is nickel concentration (mg/g) in the test solution after sorption.

Nickel concentration was determined at the wavelength of 352.454 nm. Previously the calibration curve had been constructed. To construct the calibration curve in the range of 0.5 - 5 mg/l, 3 calibration solutions were prepared by the serial dilution method: 5 ml aliquot of the standard sample (Bottle ICP-OES Wavecal conc 500 mL 500 ppm, Batch No: n6610030000) was placed in a 50 ml volumetric flask and adjusted to the mark with purified water (solution 1). Afterwards 10 ml of solution 1 was collected, transferred to a 50 ml volumetric flask and diluted to the mark with purified water (solution 2). Then 5 ml of the solution 2 was placed in a 50 ml volumetric flask and diluted to the mark with purified water (solution 3).

Method of determining the sorption of aluminium ions (III): 500 mg of BPMP was placed in a 50 cm³ flask and adjusted to the mark with aluminium nitrate solution in the following concentrations: 0.00001, 0.00002,

0.0001, 0.001, 0.003, 0.005, 0.015, 0.02, 0.1, and 0.2 mol/l. The flasks were hermetically sealed and left for 2 hours at room temperature (23±2°C). Then the suspension was filtered through the filter paper under pressure.

Aluminium percentage was determined in work standard solutions (WSS) and solutions after BPMP sorption. The concentration of sorbed aluminium in grams per one gram of the sample was determined using the formula:

$$X = (C_{WSS} - C_{TS}) * 1000 \quad (4)$$

where, C_{WSS} is aluminium concentration (mg/g) in the solutions before sorption and C_{TS} is aluminium concentration (mg/g) in the test solution after sorption.

Aluminium concentration was determined at the wavelength of 396.152 nm. Previously the calibration curve had been constructed. To construct the calibration curve in the range of 0.5 - 5 mg /l, 3 calibration solutions were prepared by the serial dilution method: 5 ml aliquot of the standard sample (Bottle ICP-OES Wavecal conc 500 mL 500 ppm, Batch No: n6610030000) was placed in a 50 ml volumetric flask and adjusted to the mark with purified water (solution 1). Afterwards 10 cm³ of solution 1 was collected, transferred to a 50 cm³ volumetric flask and diluted to the mark with purified water (solution 2). Then 5 cm³ of the solution 2 was placed in a 50 cm³ volumetric flask and diluted to the mark with purified water (solution 3).

Method of determining functional groups by IR- spectrophotometry: 5 mg of brown peat moss powder dried to a constant weight was mixed with 800 mg of potassium bromide, and the mixture was placed in the ball mill for 2 minutes. The resulting powder consisting of brown peat moss powder and potassium bromide mixture was placed on the tablet press at 200 kg/cm³. The obtained tablets were placed on the device screen. IR-spectra of the obtained samples were recorded on the TENSOR 360 Avatar FTIR ESP spectrometer (Bruker, Germany) in the transmission mode. The resolution was 4 cm⁻¹, the number of scans was 32. For convenient comparative analysis spectra of all the samples were recorded in the same mode.

Isothere adsorption parameters were evaluated according to experimental data using Fit regression function of Statistic packet in Maple Computer Algebra System

RESULTS AND DISCUSSION

In order to study the principles of sorptive removal of heavy metal ions with brown peat moss powder (BPMP), it is necessary to know physical and chemical properties of the process. The most fundamental way to describe this process is to construct an adsorption isotherm that relates the amount of adsorbed adsorbate to the adsorbate equilibrium concentration in the solution.

To interpret adsorption isotherms, we used a number of adsorption models that describe relatively well the equilibrium in adsorbate-adsorbent interaction (aqueous metal salt solution – plant-based adsorbent)

Several approaches to description of ion exchange equilibria are known. They are based on the law of mass action, Gibbs-Donnan equation and its analogues, methods of statistical physics for deriving the equilibrium equation, etc. [8, 9, 10].

The most common approach used to analytically describe ion exchange equilibria is based on the law of mass action, where heterogeneous ion exchange is considered as a reversible chemical reaction.

Distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm equations using the law of mass action, such as Nikolsky-Eisenmann equation, Langmuir equation, and Freundlich equation. The Nikolsky-Eisenmann equation adequately describes the equilibrium of single-charge cation exchange; however, to describe multiple-charge ion exchange, this equation is less appropriate. The most common model to describe isotherms of metal adsorption onto polymer materials are Langmuir and Freundlich equations [11-13]. The Langmuir model is typically used in the following form:

$$a = a_{\infty} \frac{KC}{1 + KC}$$

where K is a concentration constant of the adsorption equilibrium that characterizes adsorption intensity, l·mole⁻¹; C is the equilibrium concentration of metals in the solution; a_{∞} is fractional occupancy of adsorption sites.

The Freundlich adsorption isotherm is described by an exponential function:

$$a = KC^{1/n}$$

The Freundlich isotherm is introduced as an empirical model, and constants K and n have no physical significance. The Freundlich isotherm, as opposed to the Langmuir adsorption model, does not reflect the threshold adsorption value at saturation [14].

Sorption isotherms shown on Fig. 1 were drawn according to the experimental data. The research results have shown that the adsorption isotherm of Al³⁺ ions is described by the Freundlich model. The graph shows that adsorption increases to infinity. The adsorption isotherms of Na⁺ and Ni²⁺ ions are described by the

Langmuir model, where a monolayer of adsorbate molecules is formed on the adsorbent surface. The isotherms show a plateau, as the active sites become saturated.

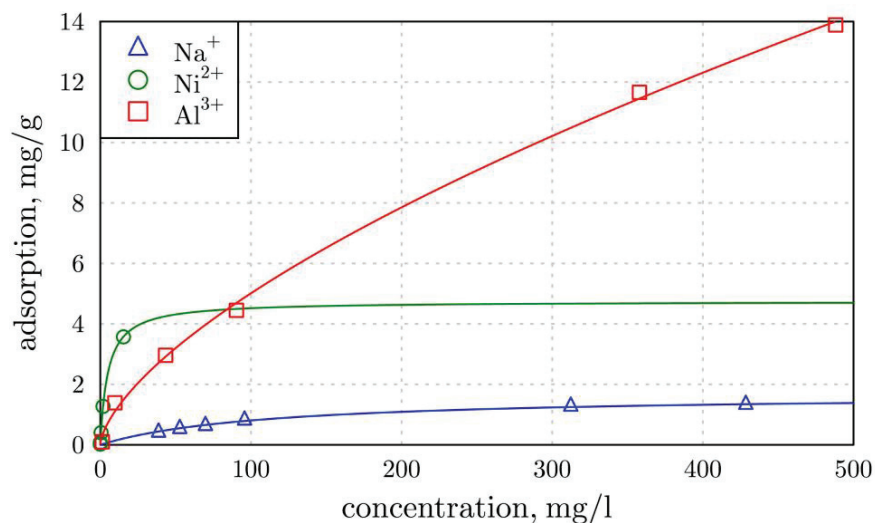


FIGURE 1. Adsorption isotherms of Al^{3+} , Na^+ and Ni^{2+}

The parameters of the adsorption equilibrium are presented in Tables 1 and 2. The adsorption equilibrium constants of the Langmuir isotropes Na^+ и Ni^{2+} are $9.15 \cdot 10^{-3}$ and $1.98 \cdot 10^{-1}$, and the limiting adsorption values are 1.68 and 4.75, respectively (Table 1). The adsorption equilibrium constants of Freundlich's isotherm are 0.253 and $1/n = 0.648$. It is obvious from Table 1 that the value of Ni^{2+} adsorption is four times higher than that of Na^+ adsorption. This may be explained by metal valency. As valency increases, the adsorption value rises.

TABLE 1 Adsorption equilibrium parameters of Na^+ and Ni^{2+}

Metal ion	Parameters	
	a_{∞}	K
Na^+	1.68	$9.15 \cdot 10^{-3}$
Ni^{2+}	4.75	$1.98 \cdot 10^{-1}$

TABLE 2 Adsorption equilibrium parameters of Al^{3+}

Model	Parameters	
	K	$1/n$
Freundlich isotherm $a = KC^{1/n}$	0.253	0.648

In previous studies the component composition of brown peat moss was determined. It consists of a polysaccharide complex (2.88%) and phenolic compounds (0.20-0.22%) [15]. Sorption activity of sphagnum mosses may be attributed to the presence of the carboxyl and hydroxyl groups in their composition. The presence of structural changes in the brown peat moss powder functional groups during nickel (II) binding is proved by the IR spectroscopy data. The IR spectra of the brown peat moss powder sample before and after nickel (II) sorption are shown in Fig. 2.

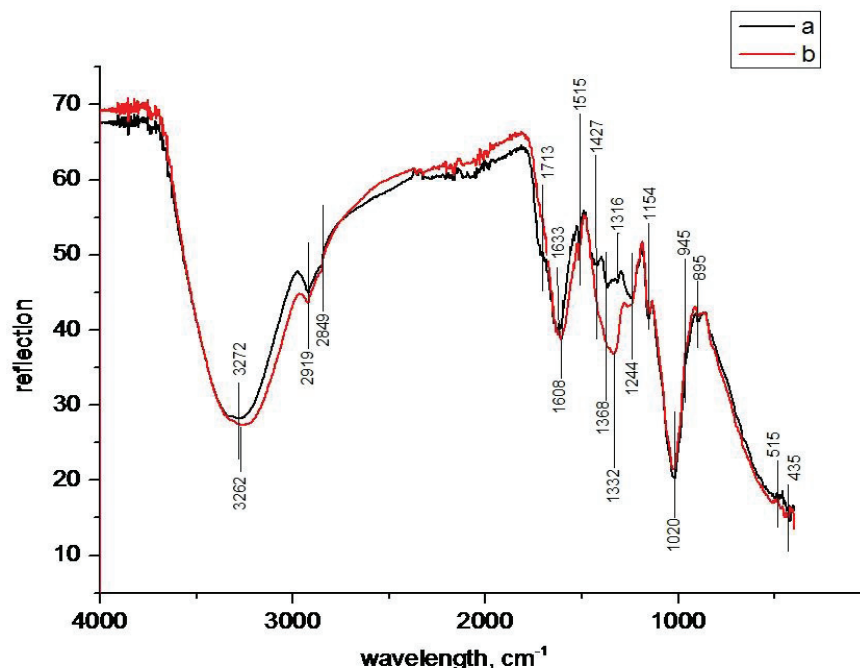


FIGURE 2. IR spectra of Brown Peat Moss Powder before Ni^{2+} sorption (b), IR spectra of Brown Peat Moss Powder after Ni^{2+} sorption (a)

Salts of carboxylic acids are characterized by the presence of absorption bands in the 1610 cm^{-1} and $1400\text{--}1300\text{ cm}^{-1}$ regions; they are observed on the brown peat moss powder sample. A broad absorption band in the $1427\text{--}1244\text{ cm}^{-1}$ region is most likely associated with ion sorption. The changes in brown peat moss powder IR spectra in the $1427\text{--}1244\text{ cm}^{-1}$ and 1713 cm^{-1} regions after sorption confirm the role of the mentioned functional groups in binding of the marker under investigation. Thus, the experimental data have confirmed that the sorption mechanism of brown peat moss powder relative to nickel (II) ions consists in both ion exchange of the carboxyl group protons for Ni^{2+} ions.

The amount of adsorbed metal ions allowed to assume that cations interact mainly with --COOH groups of BPMP according to the ion exchange reaction:



Thus, we have shown that the mechanism of Ni^{2+} ion adsorption consists in ion exchange of carboxyl group protons. Substitution of sodium ions for hydrogen protons passes through the same mechanism.

CONCLUSIONS

Studying metal ion adsorption onto brown peat moss powder allows to identify the mechanism of sorption, the nature of adsorption sites and peculiarities of their interaction with metal ions.

Thus, the adsorption isotherms of Na^+ and Ni^{2+} are described with the Langmuir model, and the adsorption isotherm of Al^{3+} is interpreted with the Freundlich equation. The adsorption equilibria constants of Langmuir isotherms for Na^+ and Ni^{2+} adsorption are $9.15 \cdot 10^{-3}$ and $1.98 \cdot 10^{-1}$, while the threshold adsorption values are 1.68 and 4.75, respectively.

IR spectra of the brown peat moss powder samples have identified important chemical bonds (carboxyl and carbonyl groups), the concentration of which plays an important role in manifestation of sorbent functional activity. The mechanism of metal ion adsorption on to BPMP is determined by adsorption and ion exchange.

REFERENCES

1. T.E. Nikiforova, V.A. Kozlov and M.V. Rodionov, *J. Applied chemistry* **7**, 1073-1078 (2010).
2. O. N. Bagrovskaya NA, T.E. Nikiforova, V.A. Kozlov and S.A. Lilin, *Physicochemistry of the surface and protection of materials* **6**, 622-626 (2010).
3. T.E. Nikiforova and V.A. Kozlov, *J. Physical chemistry* **10**, 1724-1729 (2012).
4. K. Kelly-Vargas, M. Cerro-Lopez, S. Reyna-Tellez, E.R. Bandala and J. L. Sanchez-Salas, *Physics and Chemistry of the Earth Parts A/B/C* **37**, 26-29 (2012).
5. G. Zhao, X. Wu, X. Tan and X. Wang, *The Open Colloid Sci. J.* **4**, 19-31 (2011)
6. N.V. Kelus, L.G. Babeshina and S.E. Dmitruk, *Bull. of Siberian Medicine* **4**, 37-41 (2009).
7. G. Raj, E. Balnois and C. Baley, *Int. J. Polym. Sci.* **11**, 23-34 (2011)
8. U. S. Goldfarb, V.I. Kazatchkov and E.A. Luzhniki, *Medicine* (2001).
9. N.A. Bagrovskaya, T.E. Nikiforova and B.A. Kozlov, *GOX.* **72**, 373-376 (2002).
10. N.A. Bagrovskaya, T.E. Nikiforova and B.A. Kozlov, *Chemistry and Chem. Eng.* **46**, 71-74 (2003).
11. N.A. Bagrovskaya, T.E. Nikiforova and B.A. Kozlov, *Chemistry for Sustainable Development.* **14**, 1-7 (2006).
12. V.I. Yuriev, L.G. Vinogradov and T.V. Rodina, *Chemistry* **34**, 74-78 (1982).
13. N.V. Kelus, *Key Engineering Materials* **683**, 363-369 (2016).
14. A.M. Sampiev, E. B. Nikiforova and N. A. Davitavyan, *New Technol.* **2**, 247-254 (2012).
15. V.N. Dmitruk, Author. dis. Cand. Pharm. Science, Samara, 2008.