A Method For Evaluating the Sorption Capacity of The Sorbents

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ABSTRACT: *A new method for evaluating the sorption capacity of the sorbents is offered. The proposed model is based on the adsorption data of the sorbent depending on the sorption duration in static mode. The new model allows to quickly and easily evaluate the duration of sorbent saturation. The formula of this relationship is determined by means of plotting of sorbent saturation curve on the base of experimental data, and using of Exel Trendline program. After the appropriate calculations and plotting q from time the sorption capacity of the sorbent is estimated. The model, as a primary parameter, includes time. The experimental data were obtained on the base of peat-containing sorbent for sorption of copper and cobalt. Sorption processes were evaluated by ICP-MS.*
Keywords :*sorption, desorption, adsorption isotherm, adsorption capacity.*

I. INTRODUCTION

Heavy metals, such as Ni^{+2}, Cr^{+3}, Cu^{+2}, Pb^{+2}, Cd^{+2}, etc., are often found in industrial effluents and emissions to the environment, which is a serious threat because of their acute toxicity. The acid flows with high content of heavy metals and radionuclides have a negative impact on biodiversity in aquatic systems. Traces of these elements can be presented in different forms - from the molecular dissolved and colloidal states to micron size particles [1].There are different methods (mechanical, physical-chemical, chemical and biological), which are currently used to remove heavy metals from the water. Among these physical and chemical methods of removing heavy metals from water, adsorption method is the most effective. In recent years, great attention is attached to water treatment by means of natural sorbents or sorbents derived from them [2].

Peat is an inexpensive, available sorbent for extracting a wide range of pollutants. It can be used either individually or as a component of composite sorbents and complex substances [3-5].Due to the presence of organic compounds containing polar functional groups such as alcohols, aldehydes, carboxylic acids, ketones, et al., peat has high complexing properties [6,7].Chitosan is non-toxic, biodegradable and biocompatible polymer. Chemical modification of chitosan is due to the presence of amino and hydroxyl groups therein, which makes it attractive for hybrid materials [8-11].The use of sorbents based on waste and natural materials is an important issue and is of great interest, as resource saving and environmental protection are priorities in modern science and technology, and the use of waste in industrial scales is economically feasible [12-14].The aim of this work is to study the sorption properties of the composite sorbent based on peat and chitosan for adsorption of heavy metals in static mode and evaluation of the sorption capacity of the sorbent using a new model.Development of an express new and simple model to assess the sorption capacity of the sorbents is an important issue. There are a number of models: 1 Langmuir; 2. Freundlich; 3.Temkin; 4. Dubinin-Radushkevich and others. All of these models have their advantages and disadvantages. For example, Langmuir model best describes the adsorption and largely coincides with the experimental data. Model Freundlich less coincides with the experimental data. Models Temkin and Dubinin-Radushkevich are more theoretical in nature, which cannot take into account all the factors that may affect the sorption processes. There are other models (Redlik-Petersson, Thoth). However, for the construction of isotherms in accordance with the models more effort, a lot of calculations and experimental data are necessary.

1.The equilibrium isotherms.

Equations of equilibrium isotherms are used to describe the experimental sorption data. Parameters of the equations and underlying - thermodynamic assumptions of these models, give some idea of the sorption mechanisms, surface properties and the affinity of the sorbent.Freundlich isotherm In 1906 Freundlich introduced the earliest known equation of the adsorption isotherm. This empirical model can be applied to the non-ideal sorption on heterogeneous surfaces and multilayer sorption. These data describe the empirical equation proposed by Freundlich [15,16].

$$q_e = K_f \, C_e^{1/n}$$

where: K_f - Freundlich isotherm constant (*mg/g*); n - adsorption of the intensity; C_e - equilibrium concentration of the adsorbate (*mg /l*); q_e - the amount adsorbed per gram of sorbent at equilibrium (*mg/g*).
The linearized form of the Freundlich equation can be presented as follows:

$$log\ q_e = \ log\ K_f\ + \ 1/nlog\ C_e$$

The constant K_f is an approximate indication of the adsorption capacity, while the 1/n is a function of the adsorption force

2.Langmuir Isotherm

In 1916 Langmuir developed the theoretical equilibrium isotherm, which relates the amount of gas adsorbed on the surface and its pressure. Langmuir model is probably the best known and most widely used adsorption isotherm. The model agrees well with a wide variety of experimental data. At low concentrations it obeys Henry law. Langmuir isotherm model quantitatively describes the formation of a monolayer adsorption of adsorbate on the outer surface of the adsorbent, after which adsorption no longer takes place. Thus, the Langmuir model represents the equilibrium distribution of metal ions between the solid and liquid phases. Based on these assumptions, the Langmuir isotherm can be represented by the following equation [16,17]:
Langmuir adsorption parameters can be determined using the Langmuir equation in the linearized form.

$$q_e = q_m K_L C_e/(1+K_L C_e)$$

where:C_e - equilibrium concentration of the adsorbate (mg/l); q_e - amount of substance adsorbed per gram of adsorbent at equilibrium (mg/g); q_{max} - the maximum capacity of the monolayer coating (mg/g);
K_L- Langmuir isotherm constant (*l/mg*).
Meaning q_{max} and K_L were calculated from the slope and the intersection point of a Phase $1/q_e$.

3.Temkin Isotherm

Temkin adsorption isotherm model contains a factor that takes into account the interaction of adsorbate with the adsorbent. Ignoring the extreme low and high concentrations, Temkin isotherm suggests that the drop in the heat of sorption is linear, not logarithmic, as implied in the Freundlich equation [18,19]. The measurements were carried out putting the amount of sorbed q_e against lnC_e. The constants were determined from the slope and the point of intersection. The model is given by the following equations:

$$q_e = (RT/b_T)x \ln (\ A_T C_e)$$
$$q_e = \ (RT/b_T)x \ln A_T + (RT/b_T)x \ln C_e$$
$$B = RT/b_T$$
$$q_e = \ B\ln A_T + B \ln C_e$$

where: A_T - binding constant equilibrium isotherms Temkin (*l/g*); b_T - constant Temkin isotherm;R - universal gas constant (8.314 $J.mol^{-1}K^{-1}$); T - temperature at 298 K; B - Constant associated with the heat of adsorption (J/mol).

4. The Dubinin-Radushkevich isotherm [20-21]

Isotherm, Dubinin Radushkevich usually used to express the adsorption mechanism with a Gaussian distribution of energy on the heterogeneous surface.

$$q_e = (q_m)exp\ (-K_{ad}\varepsilon^2)$$
$$\ln q_e = \ln(q_m)- (K_{ad}\varepsilon^2)$$

where q_e - the amount adsorbed in the adsorbent in the equilibrium (*mg/g)*; q_m - theoretical saturation isotherm capacity (*mg/g*) ; K_{ad} - constant isotherm Dubinin-Radushkevich (*mol^2·kJ^{-2})*; ε - constant isotherm Dubinin-Radushkevich.

Approach is generally used for distinguishing physical and chemical adsorption of metal ions from its mean free energy E per molecule adsorbent, which can be calculated using the relationship:
$E = [\ 1/(\sqrt 2 B_{DR})]$

where B_{DR}, denoted as a constant isotherm. At the same time, ε parameter can be computed as:
$\varepsilon = RT \ln [\ 1+1/C_e]$

where: R = the universal gas constant (8.314 $J.mol^{-1}K^{-1}$); T - absolute temperature (K); C_e - equilibrium concentration of the adsorbate (mg/l).
One unique feature of the model Dubinin-Radushkevich isotherm lies on the fact that it depends on temperature.

5. Redlich-Peterson isotherm

The proposed Redlich and Peterson (1959) model includes features of both the Langmuir and Freundlich equations [22]. It can be described as follows:

$$qe = KRCe1 + aRCbRe$$

At low concentrations, the isotherm Redlich-Peterson is close to Henry's law, and at high concentrations, the behavior is close to the Freundlich isotherm.

6. Toth isotherm

Derived from potential theory, this isotherm [22] proved to be useful in describing the adsorption in heterogeneous systems such as phenolic compounds on carbon. It can be presented in the following equation:

$$qe = KtCe(at + Ce)1/t$$

This involves an asymmetric quasi-Gaussian distribution of energy with extended left side, i.e. most sites have an energy adsorption is less than average.

Experimental Section

To demonstrate the proposed model, the following experiments were carried out to the sorption of copper and cobalt on the peat-containing sorbent in a static mode.

Preparation of the test solution. Model aforementioned metal salt solution was prepared by dissolving the corresponding metals in distilled water. Assays were performed by ICP-MS. Analytical class reagents Were used (Aldrich Chemicals). Solutions of copper (II) sulfate ($CuSO_4 \bullet 5H_2O$) (670 *mg/l*) and cobalt chloride, $CoCl_2.6H_2O$ (19.5 *mg/l*) were prepared in deionized water.

Adsorbent - The experiments were carried out on peat - containing sorbent. Peat was taken from Vardenis (Gegharkunik region, Armenia). Peat was washed and then was dried at a temperature of 105 ± 5 ∘C for 8 hours and finally sieved to obtain a particle size range of 0.5 -1.0*mm* before use. Thereafter, for modification of the surface of the peat to the resulting peat powder 3% - chitosan solution acidified with citric acid (100*g* of peat- 90*ml* chitosan solution) was added. After exposition of peat powder in said solution for 3 hours the pH of the slurry is raised with NH_4OH to 8.5-9.0. Before that formalin was added to the suspension for the purpose of cross-linking of chitosan. The amount of formalin was 1.5-2.0% of the total volume of the suspension. It was maintained like this during 16-20 hours, then the mother liquor was removed by filtration, and the resulting mixture was washed with distilled water until neutral. After that, the filtered powder was dried at 105 ± 5°C to constant weight. The result is a peat sorbent modified by chitosan.

Experimental system - Sorption processes were carried out in a static mode on Jar-Test flocculator in mixing mode 80 rpm. The adsorbent was suspended in 800 *ml* of model solution.

The following experiments were carried out:

- Change the weight of the sorbent - 0.5*g*, 1.0*g*, 2.0*g*, 4.0*g*;

- By changing the exposure time (5*min*, 15*min*, 30*min*, 60*min*, 180*min*, 300*min*), based on single sample.

The first type of experiments aimed to evaluate sorption capacity of sorbent by means of Langmuir model on the basis of experimental data. The second type of experiment is aimed to demonstrate our proposed model.

II. RESULTS AND DISCUSSION

The new model of the adsorption capacity of sorbents. Our proposed model is much simpler and does not require a lot of calculations. The bases of this model can be presented in the following assumptions. It is well known that the amount of the adsorbed adsorbate is calculated by the following formula:

$q=V(C_o-C)/m$ (1)

where: C_o- initial concentration in *g/l; C* equilibrium concentration (*g/l*); *V* - volume of solution (*l*);
m - mass of sorbent (*g*).

Converting the (1) formula, we get the following:

$$q/C_o=V/m(C_o-C)/C_o, \quad q/C_o=V/m(1- C/C_o),$$

$q = VC_o/m(1- C/C_o)$ (2)

In this case, consider changing of the C/Co as a function of time (time of exposure to the sorbent solution) in static mode. To do this, measure the value of C is measured at regular intervals and constructed curve established equilibrium concentration from time is determined by a formula of this relationship using Exel Trendline. the value q is determined by means of placing the value C/Co in the equation (2).

$$q=VC_o/m [1 - C/C_o(t)] (3)$$

i.e., there is a dependence of q from t. From the values of t the values of q is determined, then the curve of dependence of q from t is built, and based on this the adsorption capacity of the sorbent is evaluated.

The dependence of the function $C/Co = f(t)$ can be different and the function where R^2 has the maximum value is chosen. In general, these functions are logarithmic, exponential or power-law.

The proposed model has the following advantages:

- Simplicity of calculations;
- Sorption dependence on time is used, which allows use of a single sample of the sorbent, i.e. to evaluate the sorption capacity a small amount of sorbent is required, which reduces the time and reagents to conduct experiments;
- Modeling of sorption dynamics from the point of view of sorbent saturation, depending on the time and the initial concentration of adsorbate. It is allowed to optimize choice of sorbents in the sorption processes.The proposed method is based on the experimental data only and does not account for many factors affecting the sorption processes (temperature, pH, and pore sizes etc.).

Figure 1: shows the experimental data for the adsorption of copper ions on the peat-chitosan from an aqueous solution of copper sulfate.
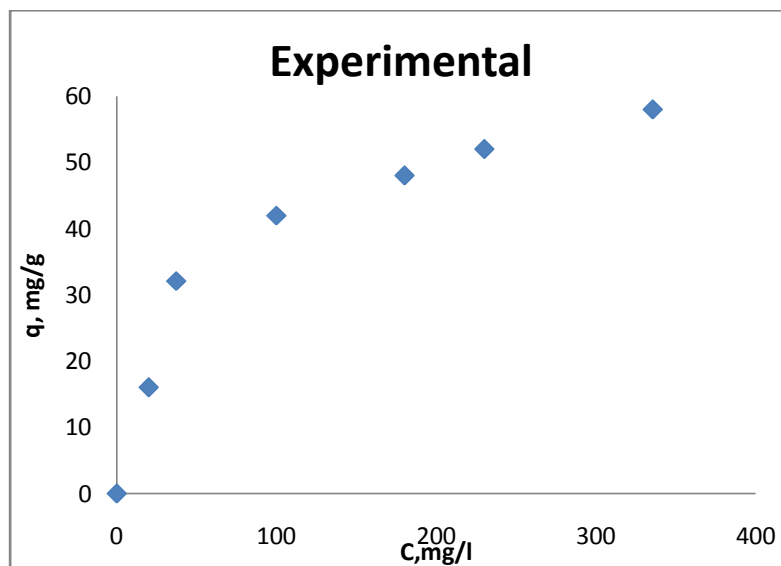
Figure S1. Sorption of copper on the peat-chitosan sorbent,(Experimental data).
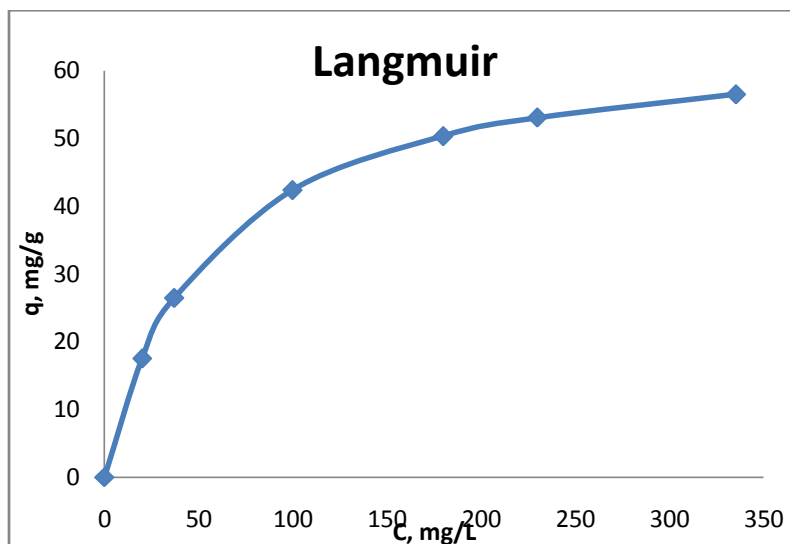
Figure S2. Sorption capacity of the peat-chitosan sorbent (Langmuir model).

From Figure 1S it follows that the maximum adsorbed copper per 1 g of sorbent is about 60 mg/g. To evaluate the sorption capacity of the sample on the basis of corresponding experimental data the Langmuir

model was used. On Figure 2 the Langmuir adsorption isotherm is shown. From Figure 2S it is seen that the Langmuir model describes these experimental data quite accurately. It appears that the sorption capacity of the sorbent for copper is about 60 *mg/g*.Figure S3 depicts a curve showing the dynamics of copper sorption on above mentioned sorbent (according to the second type of experiment).
From

Figure 3 it follows that the dependence of the C /Co from the t is as follows:

$$y = 0.025\ ln(x) + 0.5791,\ i.e.\ C/C_o = 0.025\ ln(t) + 0.5791$$

Accordingly, calculations to determine the sorption capacity of sorbent are carried out using Equation (3). The calculation scheme is shown in Table 1 and on the basis of data obtained creating the curve of *q* vs *t*. From FigureS4 it is seen that the dynamics of the saturation of the sorbent can be presented by the following formula:

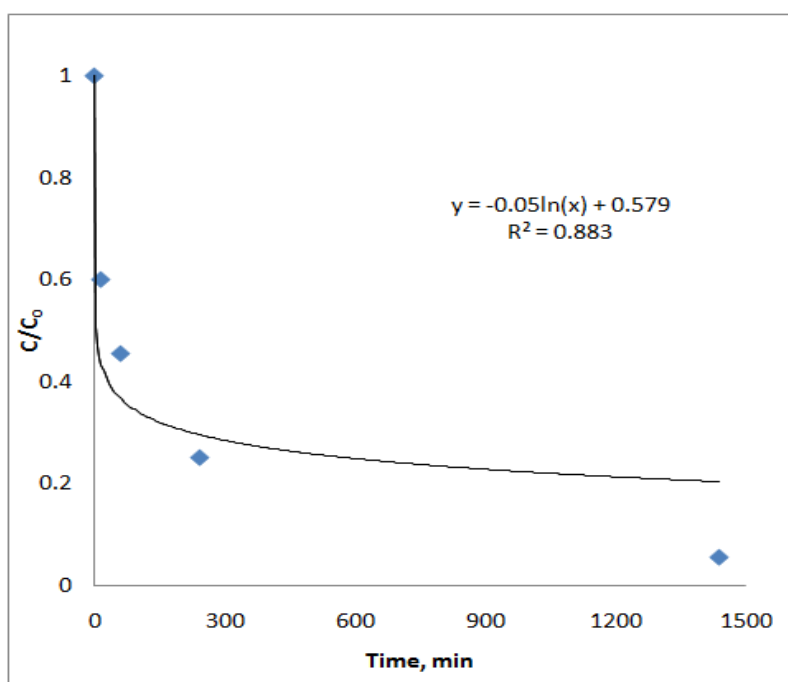$$y = 3.2876\ ln(x) + 29.86,\ i.e.\ q = 3.2876\ ln(t) + 29.86$$

Figure S3. Dynamics of copper sorption on peat - chitosan sorbent

$$q=VC_o/m\ (1 - (- 0{,}052ln(x)+0{,}5791),\ m=1g,\ V= 100ml,\ Co=680mg/l,\ VC_o/m = 68$$

Table S1 The scheme of calculating the sorption capacity of the sorbent by time

| t	q	ln(x)	0,052ln(x)	0,4209+0,052ln(x)
0	0			
5	34,31204	1,6094	0,083689	0,504589
15	38,19704	2,7081	0,140821	0,561721
30	40,64784	3,4012	0,176862	0,597762
60	43,09864	4,0943	0,212904	0,633804
180	46,98365	5,193	0,270036	0,690936
300	48,78984	5,7038	0,296598	0,717498
600	51,24064	6,3969	0,332639	0,753539
1440	54,33641	7,2724	0,378165	0,799065
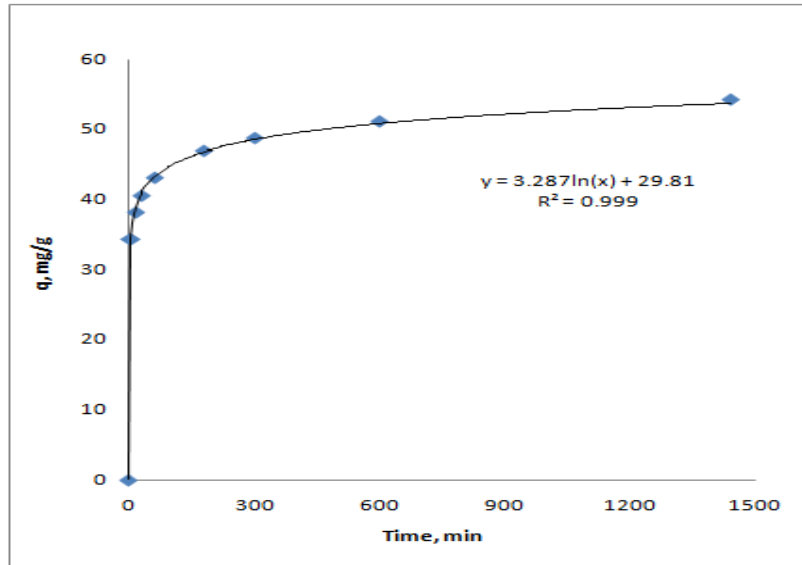
Figure S4. The saturation of peat - chitosan sorbent with the copper.Sorption capacity by time.

The sorption capacity of the sorbent, calculated in accordance with Figure S4 is 56.3 *mg/g*, whereas the adsorption capacity of the sorbent by Langmuir model is 58.0*mg/g* (Figure S2), indicating that the coincidence of data is quite high. The difference is in the range of 3%, indicating the reliability and accuracy of the proposed method for evaluation of sorption capacity of sorbents. As mentioned above, the Langmuir model best describes the experimental data, so it is more appropriate to compare the calculations of the proposed method with the Langmuir model.

Evaluation of sorption capacity of the sorbent according to the proposed method may last a maximum of 30-40 hours from the viewpoint of the experiments, in addition, one portion of sorbent is used .. The usual practice is using at least 5 batches to determine the sorption capacity of the sorbent. Meanwhile these batches are not adjusted to the saturation of adsorption, so there may be some inaccuracies in the interpretation of data obtained from multiple samples to assess the sorption properties of the sorbent. The most appropriate data can be obtained when the batches are saturated.

As mentioned above, the dependence of C/C_o on time can be expressed by different functions. In the case of copper, this dependence is described by an exponential function. In the case of cobalt dependence of C/C_o of the exposure time in solution sorbent power function (Figure 5). The above calculations to determine the saturation of the sorbent (sorption capacity of the sorbent) have been carried out on the basis of the equation $C/C_o = 0{,}4449t^{-0{,}172}$. The calculations are performed according to the scheme presented in Table 2 and the formula $q = VC_o /m (1 - 0{,}4449t^{-0{,}172})$.
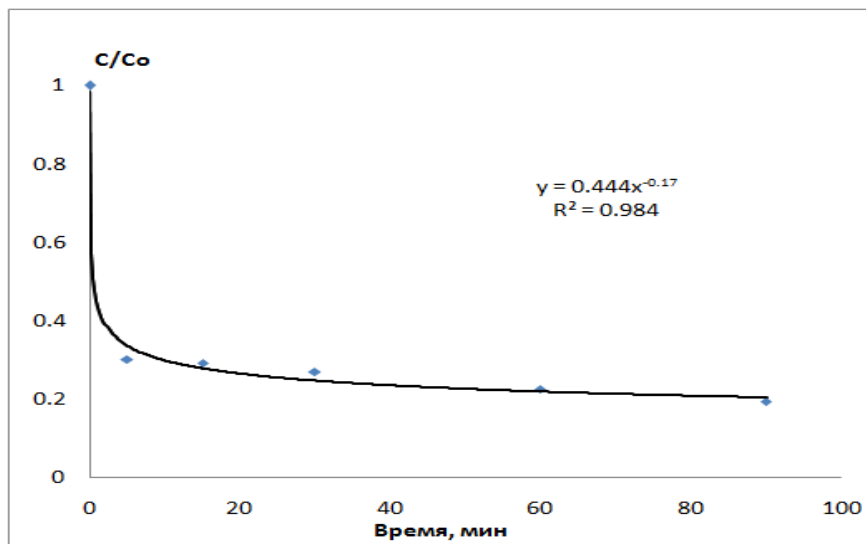

Figure S5. Dynamics of cobalt sorption on peat - chitosan sorbent

$q=VC_o/m\ (1-0,4449t^{-0,172})$, $m=4g$, $V=800ml$, $C_o=19.5mg/l$, $VC_o/m=3,9$.

TableS2.Calculation scheme of the sorption capacity of the sorbent by time

t	q	$t^{-0,172}$	$0,4449t^{-0,172}$	$1-0,4449t^{-0,172}$
0	0			
5	1,12	0,7582	0,337323	0,662677
15	1,340652	0,6276	0,279219	0,720781
30	1,398992	0,5571	0,247854	0,752146
60	1,450794	0,4945	0,220003	0,779997
180	1,521299	0,4093	0,182098	0,817902

Figure S6 shows the sorbent saturation curve with cobalt as against time exposure. It follows from Figure S6 that the sorption capacity of the sorbent for cobalt is about 3.3 *mg/g*.
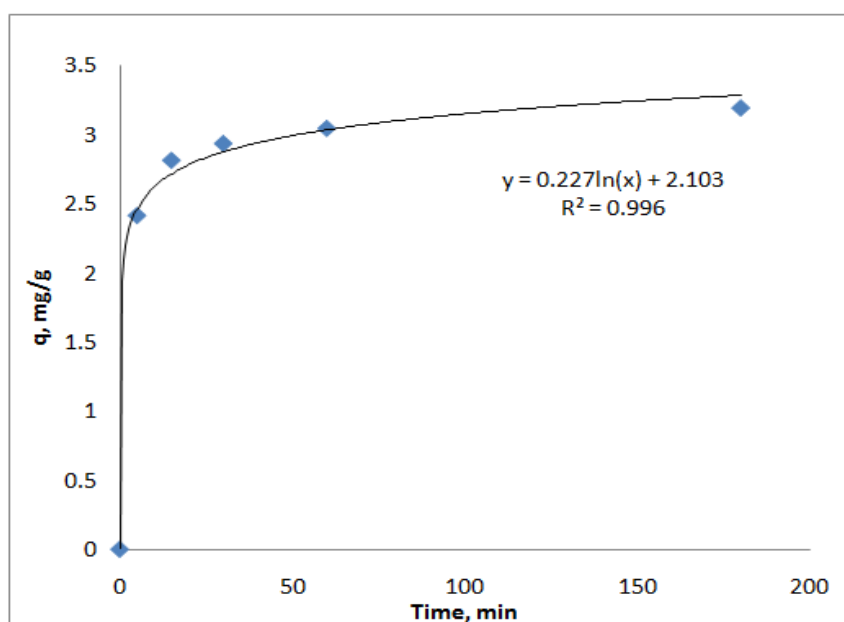
Figure S6. The saturation of peat - chitosan sorbent with the cobalt.Sorption capacity by time.

Summary and Conclusions

New method for rapid and easy determination of the sorption capacity of the sorbents is developed. The possibility of tracking of the saturation of the sorbent is given, which allows determining the processes and timing of replacement of the sorbent when it is saturated. This is important in the design of the various processes associated with the sorption. The knowledge of the dynamics of sorbent saturation and sorption capacity of the sorbent is important for the design of the particular manufacturing processes.

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