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Original Research

Biosorption of Cr(III) Ions by Wheat Straw and Grass: a Systematic Characterization of New Biosorbents

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Abstract

Recently, increased interest in the application of various biosorbents in metal ions removal has been observed. The paper presents a systematic characterization of new and commonly abundant low-cost biosorbents: above-ground plant parts of wheat straw and grass. Cr(III) was chosen as a model sorbate. The effect of the most significant process parameters (temperature, pH, initial concentration of Cr(III) ions on kinetics, as well as temperature and pH) on biosorption equilibrium was studied. Biosorption was found to be a quick process. The equilibrium was reached within 10-20 minutes. Biosorption capacity of the studied sorbents was intermediate when compared with other sorbents of plant origin ca. 20 mg/g, but since these materials are commonly abundant and of minimal cost, it is possible to improve wastewater treatment efficiency by increasing the concentration of the sorbent.

The kinetics of the process in the case of both biomaterials was described with pseudo-second order equation and the equilibrium of biosorption by wheat straw was described with the Freundlich equation and by grass with the Langmuir model. The above equations were chosen to achieve the best consistency of experimental data with the model results. Also, the mechanism of biosorption was investigated, and was determined to be physical adsorption.

The paper also discusses the possible methods of utilization of metal-laden biomass, including non-destructive elution with the regeneration of the biosorbent and ashing as the method of destruction and further concentration of metal.

Keywords: biosorption; wheat straw; grass; sorption kinetics; physical sorption; Ion-exchange

Introduction

Recently, particular interest in the application of the biosorption process in the treatment of large volume, low contaminant level effluents has been observed [1-5]. There are two classes of biosorbents available: those that possess very high biosorption capacity but need to be specially propagated (e.g. *Spirulina sp.* [6])) and those that possess intermediate biosorption capacity but are of no cost and are commonly abundant (e.g. *Saccharomyces cerevisiae* [7]).

In the past, biosorption was defined as the process performed by non-living microbial biomass. However, recently the definition widened and covers also other biomaterials, including algae, fungi, biomasses of plant and animal origin. While microbial, algal and fungal biomass has been thoroughly studied, only a few report systematic biosorption characteristics of plant and animal biomasses

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[8-9]. Low-cost sorbents that were characterized in the literature include root tissues of common weeds *Amaranthus spinosus* and *Solanum nigrum* for the removal of Cu(II) ions [10-11], wheat straw corncobs and barley husks for the adsorption of dyes [12-14], brown seaweed *Ecklonia maxima,* dealginated seaweed waste, alginate fiber and waste linseed fiber to remove Cu, Ni and Cd ions from solutions [15-16], cork biosorption in the removal of heavy metals (Cu, Zn, Ni) [17], strontium ion biosorption by plant root tissue [11], sorption of metal ions to the biomass of various aquaphytes [2], removal of dyes from textile dye effluent by apple pommace and wheat straw [12-14].

The literature does not include much information on biosorption of metal ions by the above-ground parts of commonly abundant plants. Therefore, in the present work a basic characterization of two biosorbents of plant origin, wheat straw and grass, was performed. An example metal ion used in the experiment was Cr(III) ions. The effect of process parameters: initial concentration of Cr(III) ions, temperature and pH on process kinetics and the effect of temperature and pH on process equilibrium were investigated. Mathematical models for the description of both process kinetics and equilibrium were proposed. Also, the mechanism of the process was studied

Experimental Procedures

Sorbent Preparation

Wheat straw was harvested from an agricultural farm in Little Poland region (Poland) and grass was harvested from the campus of Wrocław University of Technology (Poland). The biomasses were washed with tap water several times and afterwards with redistilled water for three times. Then they were transferred to the oven to dry at 50°C. The dried materials were crushed and milled. The average size of the material was 100 µm. No storage problems were observed. The material was furtherly used in biosorption kinetic and equilibrium experiments. Also, its physical sorption characteristics and ion-exchange capacity was investigated.

Batch Sorption Experiments

The experiments were performed in 250 ml Erlenmeyer flasks containing 100 ml of chromium(III) solution (prepared from $Cr(NO_3)_3(9H_2O$ from POCh S.A. Gliwice) and sorbent at a concentration of 5 g/L in thermostated water bath shaker at 150 rpm. Samples of sorbent suspension (5 ml) were taken to determine residual concentration of chromium(III) in the solution. Before analysis, samples were filtered through No. 2 filter paper. The procedure of determination of specific surface area as well as cation exchange capacity was described elsewhere [6].

Sorption capacity was determined from the mass balance. The correctness of such an approach was confirmed by the analysis of the biomass.

Analytical Methods

The concentration of metal ions in the samples was determined by Inductively Coupled Plasma Spectrometry ICP-AES plasma spectrometer (Philips Scientific PU 7000). The samples were analyzed three times (the relative standard deviation of the measurement did not differ from the acceptable for Certified Reference Materials). The value of standard deviation of reproducibility for CRM and experimental results was 1.9%. pH measurements were conducted with a Mettler Toledo MA235 pH/ion analyzer. Potentiometric titration was employed in determination of ion-exchange capacity, according to the method described previously [6].

Results

In the literature there has been a significant amount of research on biosorption and there are various approaches for the characterization of biosorbents. A multitude of investigation techniques sometimes makes it difficult to compare findings of various authors. Therefore, there is a need to propose a standardized procedure of biosorbents characterization. The present work reports an approach of systematic characterization of two low-cost biosorbents: wheat straw and grass.

Biosorption Kinetics

The paper presents studies on the effect of initial concentration of Cr(III) ions, temperature and pH on kinetics of biosorption of Cr(III) ions by wheat straw and grass (Fig. 1-3). In both cases it was found that the process was rapid. The equilibrium was reached within 10 to 20 minutes. The applicability of various kinetic models to describe the process was tested, including first-order, second-order, pseudo first-order, and pseudo second-order equations. The values of coefficient of determination of the models were compared. Clearly, the highest values of the coefficient (R^2>0.927 for wheat straw and R^2>0.993 for grass) were denoted in the case of pseudo-second order equation and this model (1) was furtherly used to describe the process kinetics.

$$\frac{dq}{dt} = k(q_{eq} - q)^2 \quad (1)$$

The model parameters were determined by a linearization method [18-19]. The model possesses two model parameters q_{eq}, representing equilibrium biosorption capacity and k representing the rate constant of the process. Sorption capacity of wheat straw was usually slightly higher than grass (15-20 mg/g), but the rate of the process was higher for grass when compared with straw (Fig. 1-3, Table 1).

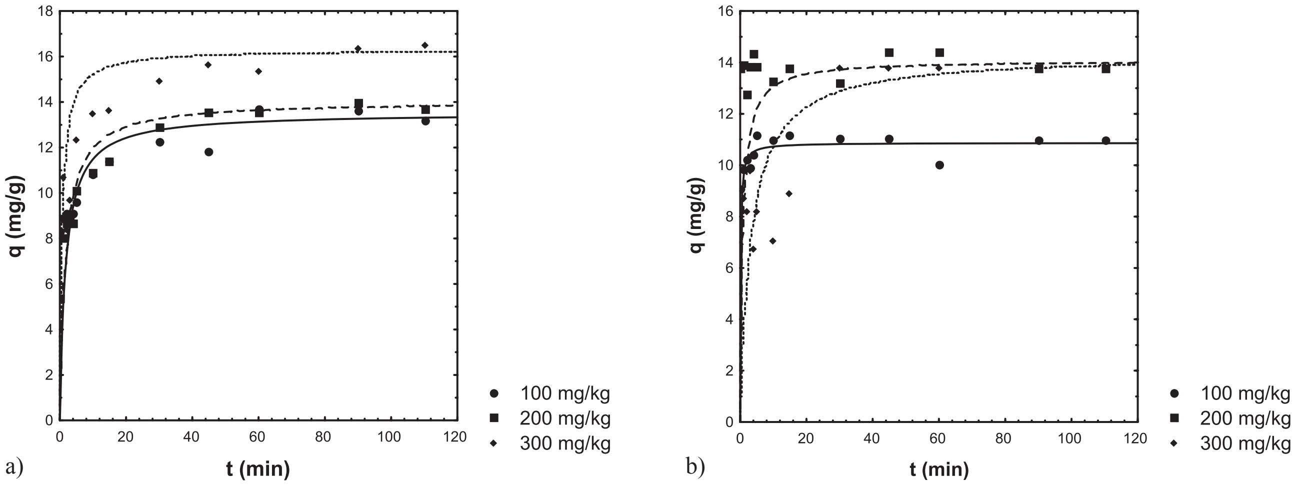
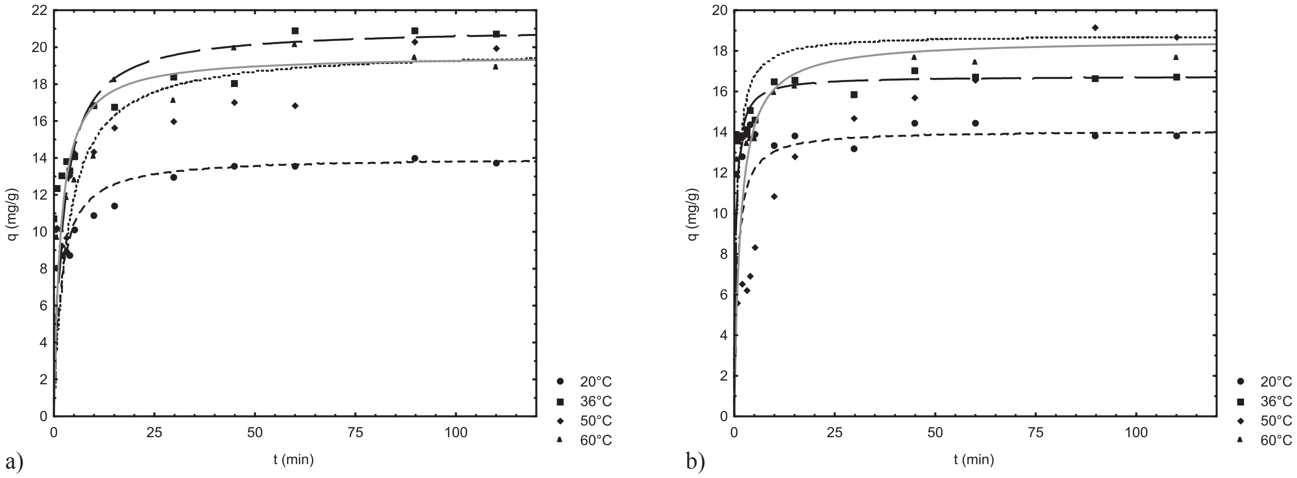


Fig. 1. Effect of initial concentration of Cr(III) ions in the solution on sorption kinetics (T 20 oC, pH 5, CS 5 g/l) by wheat straw (a) and grass (b).



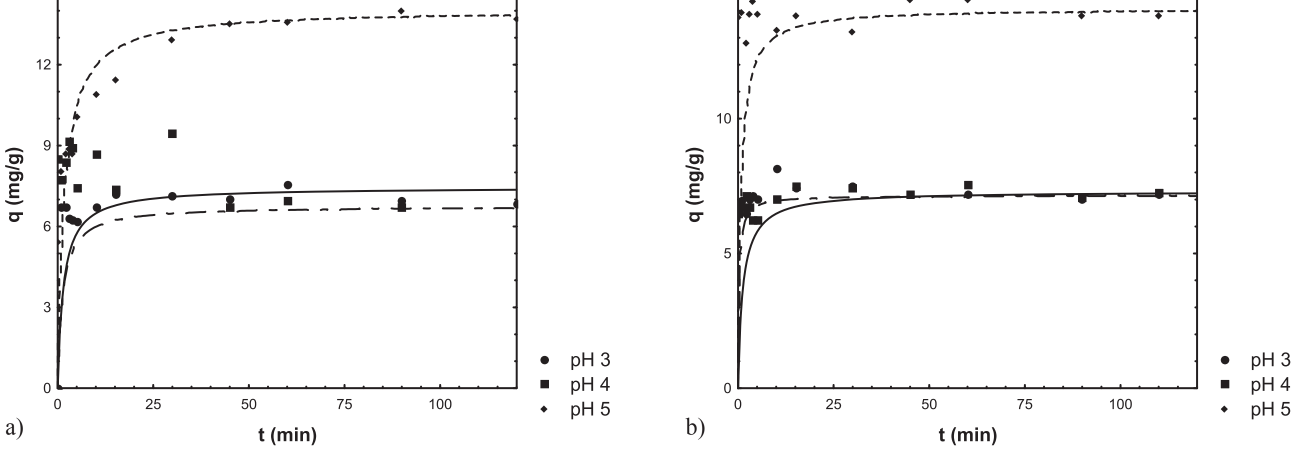


Fig. 3. Effect of pH on sorption kinetics (C0 200 mg/kg, T 20 oC, CS 5 g/l) by wheat straw (a) and grass (b).

Table 1a. A comparison of second-order adsorption rate constants at different initial Cr(III) concentration (T 20°C, pH 5.0, C_S 5.0 g/l) for biosorption by wheat straw and grass.

C_0 (mg/kg)	Wheat straw			Grass		
	q_{eq} (mg/g)	k (g/(mg min))	R^2	q_{eq} (mg/g)	k (g/(mg min))	R^2
100	13.5	0.0415	0.997	10.9	0.682	0.998
200	14.0	0.0406	0.998	14.1	0.0902	0.994
300	16.3	0.00851	0.927	14.3	0.0210	0.993

Table 1b. A comparison of second-order adsorption rate constants at different temperatures (C_0 200 mg/kg, pH 5.0, C_S 5.0 g/l) for biosorption by wheat straw and grass.

T (°C)	Wheat straw			Grass		
	q_{eq} (mg/g)	k (g/(mg min))	R_2	q_{eq} (mg/g)	k (g/(mg min))	R^2
20	14.0	0.0406	0.998	14.1	0.0902	0.994
36	21.0	0.0211	0.997	16.8	0.152	0.999
50	19.9	0.0150	0.991	18.8	0.0871	0.998
60	19.6	0.0315	0.998	18.6	0.0357	0.994

Table 1c. A comparison of second-order adsorption rate constants at different pH (C_0 200 mg/kg, T 20°C, C_S 5.0 g/l) for biosorption by wheat straw and grass.

p_H	Wheat straw			Grass		
	q_{eq} (mg/g)	k (g/(mg min))	R_2	q_{eq} (mg/g)	k (g/(mg min))	R^2
3	7.75	0.0901	0.985	7.15	0.495	0.999
4	6.75	0.112	0.993	7.31	0.106	0.995
5	14.0	0.0406	0.998	14.1	0.0902	0.994

It was found, as expected, that an increase of the initial concentration of Cr(III) ions resulted in increased sorption capacity. However, differences between the two studied materials were observed (Fig. 1, Table 1). In the case of grass, the plateau was reached above an initial concentration of Cr(III) ions (C_0) of 200 mg/kg. In the case of wheat straw the plateau was not reached within the studied range of C_0. This suggests that when describing the equilibrium of the process, a Langmuir equation should be employed for grass and Freundlich equation for wheat straw. The presented results showed that the value *k* for wheat straw did not depend on the initial concentration of Cr(III) ions, but in the case of grass the value *k* decreased with an increase of C_0. It was found that biosorption capacity of wheat straw and grass increased with an increase of temperature. For wheat straw, the plateau was reached above 30°C, for grass above 50°C. The rate of the process decreased with an increase of the temperature. This suggests that biosorption of metal ions does not involve energy-mediated reactions [18]. Within the studied range of temperature (20-60°C) denaturation of sorbents was not observed.

Increasing the pH resulted in the increase of sorption capacity. No differences between pH 3 and 4 were observed. At pH 5 the biosorption capacity was two times higher. Solution pH influences metal binding sites on the cell surface and also metal chemistry in water [18]. In the case of wheat straw, *k* slightly decreased with pH increase; however, in the case of grass at pH 3 the rate of the process was significantly higher when compared with pH 4 or 5.

Biosorption Equilibrium

The equilibrium of biosorption is described most frequently with two models: either the Langmuir

$$q_{eq} = q_m \frac{bC_{eq}}{1 + bC_{eq}} \quad (2)$$

or the Freundlich.

$$q_{eq} = KC_{eq}{}^{n} \quad (3)$$

In biosorbents characterization these models are chosen empirically. Frequently the authors report that simultaneously both models describe experimental data and report model parameters for Langmuir as well as for Freundlich models. The reason is that the mechanism of biosorption is rarely uniform. Usually this is a combination of chemical and physical sorption.

Also, in the present study equilibrium models were chosen to achieve the best consistence of experimental data with the model results. In this work, the isotherm plot of grass showed a clear plateau suggesting a Langmuir equation and for wheat straw the plateau was not clear, that suggested the Freundlich model. The model parameters were determined by linearization. The Freundlich model was found to better fit the experimental data of sorption by wheat straw (R^2>0.979) and the Langmuir for grass (R^2>0.964) (Figs. 4 and 5, Table 2). These results were consistent with the equilibrium results of kinetic experiments performed at different initial concentrations of sorbate. The values of R^2 for Langmuir equation and wheat straw and Freundlich for grass were below 0.9.

The effects of temperature and pH were investigated. The effect of temperature was studied at two different pH values: 3 and 5. The combination effect of these two process parameters was observed. For wheat straw, increasing temperature resulted in an increase of K (the parameter of Freundlich model) at pH 3 and 5, but at pH 3, this effect was stronger. A similar effect was observed in the case of the second parameter of Freundlich equation (n). An increase of both K and n stands for increase of sorption capacity.

In the case of grass, the temperature increase resulted in an increase of q_m (the parameter of Langmuir equation) only at pH 5. This effect was particularly visible above 36°C. Temperature, however, did not affect the sorption

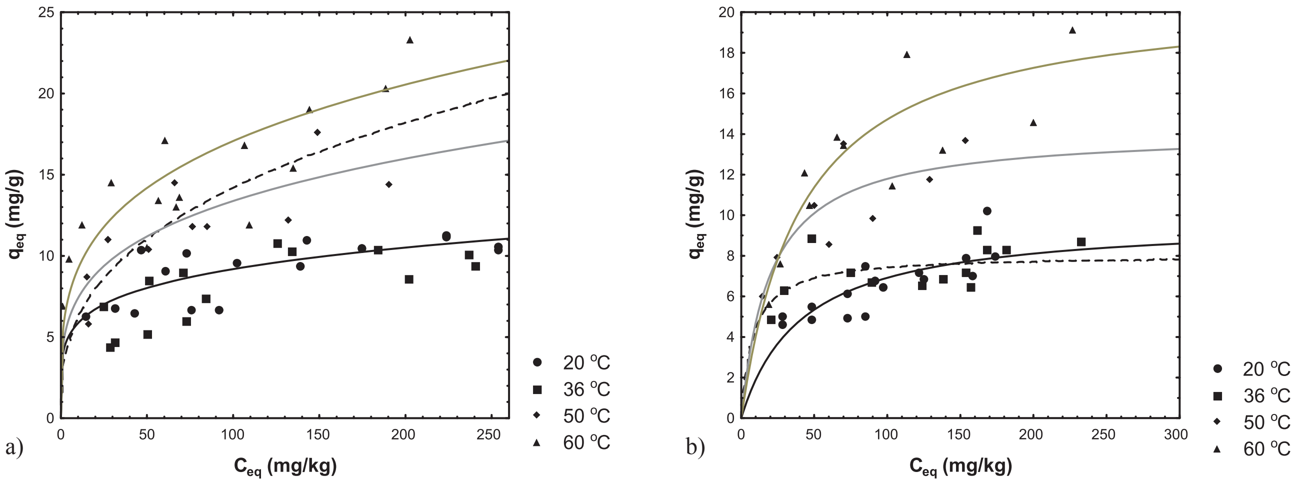


Fig. 4. Effect of temperature on biosorption isotherms at pH 5 by wheat straw (a) and grass (b).

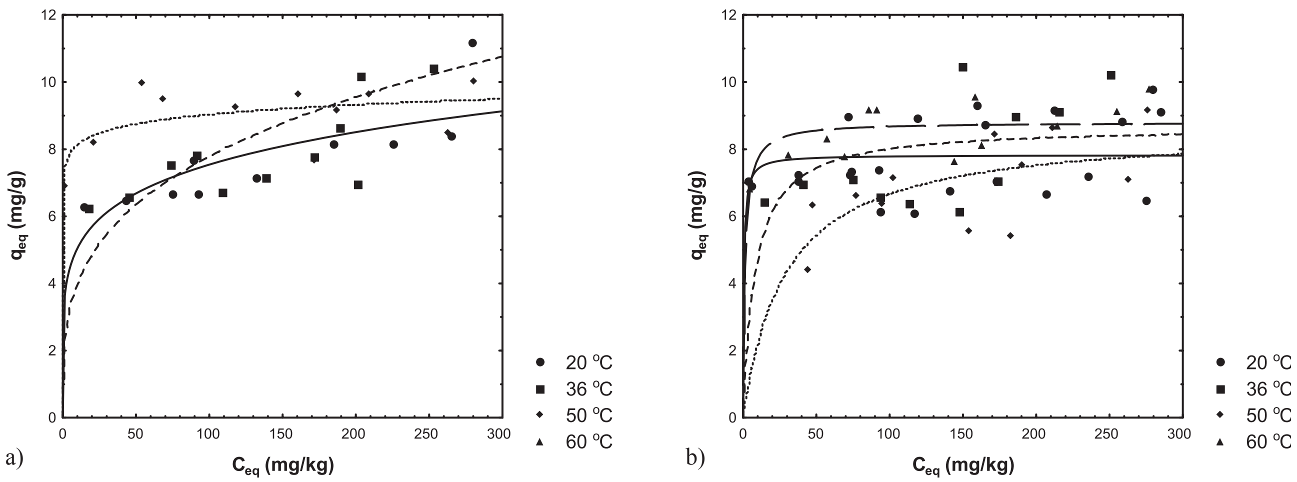


Fig. 5. Effect of temperature on biosorption isotherms at pH 3 by wheat straw (a) and grass (b).

capacity at pH 3. This could mean that biosorption is the combination of various processes. At pH 5, ion-exchange can play a significant role, while at pH 3 the significance of this mechanism decreases, since cation-binding functional groups present on the cell wall are protonated. The second model parameter, *b*, generally increased with temperature. This effect was observed above 50°C and was stronger at pH 5.

Table 2 A comparison of the model sorption constants obtained for the equilibrium model proposed at different temperatures and pH.

a) wheat straw (Freundlich equation)

T (°C)	pH	K (mg/g)/(mg/L)n	n	R^2
20	5	3.75	0.194	0.985
36	5	2.72	0.359	0.967
50	5	4.10	0.257	0.979
60	5	4.98	0.267	0.968
20	4	6.65	0.0872	0.991
20	3	3.38	0.174	0.987
36	3	2.00	0.295	0.962
50	3	7.32	0.0457	0.993

b) grass (Langmuir equation)

T (°C)	pH	qm (mg/g)	b (kg/mg)	R^2
20	5	9.80	0.122	0.981
36	5	8.03	0.104	0.985
50	5	14.2	0.0245	0.983
60	5	20.8	1.76	0.974
20	4	9.53	0.121	0.994
20	3	7.83	0.0344	0.980
36	3	8.67	0.0245	0.964
50	3	8.63	0.0500	0.977
60	3	8.80	0.699	0.994

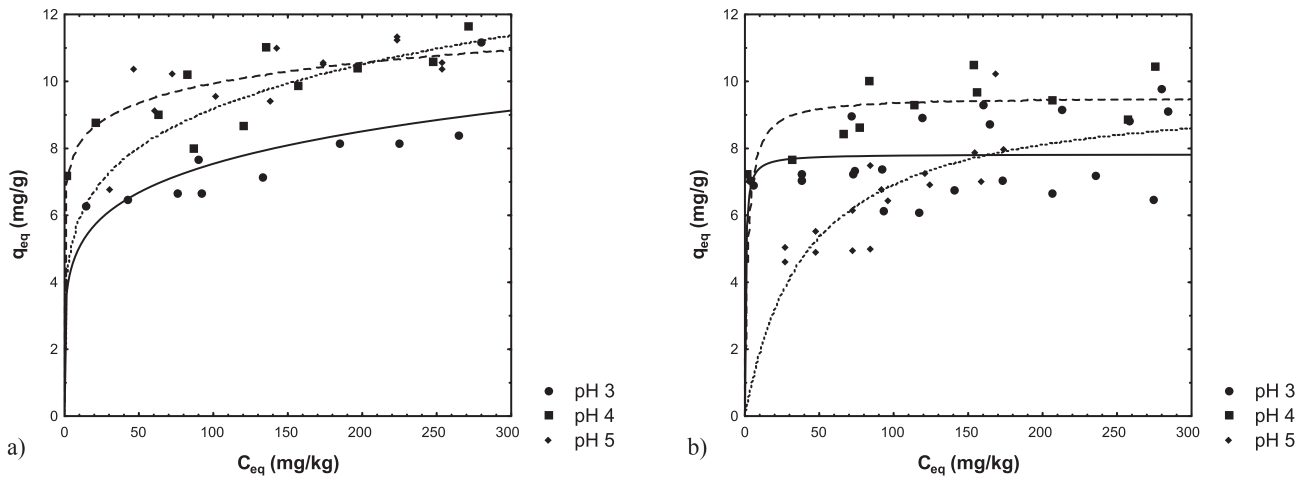


Fig. 6. Effect of pH on biosorption isotherms at pH 20°C by wheat straw (a) and grass (b).

Mechanism of Biosorption

Two mechanisms of biosorption were considered: physical adsorption and ion-exchange. The contribution of the first mechanism was investigated through determination of adsorption surface area, with the use of methylene blue, according to the procedure described previously [6]. It was found that the surface area of grass was 8.50 m^2/g and wheat straw 18.6 m^2/g. It was assumed that Cr(III) ions are bound in monolayer and on the basis of the knowledge of ionic radius [6] it was calculated that theoretical maximum biosorption capacity via physical adsorption for grass was 49.1 mg/g and wheat straw 108 mg/g. These values were higher than experimentally determined q_m for Cr(III) ions from biosorption isotherms (20-25 mg/g). Therefore, it is supposed that physical adsorption and possibly surface precipitation could contribute in the mechanism of biosorption by wheat straw and grass.

Potentiometric titration was employed in determination of ion-exchange capacity [6]. Unexpectedly, it was found that the volume of titrant used in the titration of sorbents suspension in water was lower when compared with titration of water itself. On this basis it was concluded that the mechanism of biosorption by wheat straw and grass was not ion-exchange. The above phenomenon can be explained in that the sorbent bound some of the ions present in water via physical adsorption, thus decreasing ionic strength of the solution and therefore resulting in decreased volume of titrant used in potentiometric titration. This is consistent with the findings of other authors [11] that cellulose itself, the main component of wheat straw and grass, showed very low maximum sorption capacity (0.5 mg/g Cu). This showed that other constituents of the cell wall were responsible for metal-binding properties of these biomaterials.

Discussion of Results

The present work is an example of a systematic approach toward characterization of new low-cost and commonly abundant biosorbents: wheat straw and grass. Biosorbent characterization on the example of Cr(III) ions as sorbate, included investigation of kinetics, equilibrium and the mechanism of biosorption. The effect of process parameters (temperature, pH, and initial concentration of Cr(III) ions) on kinetics, as well as temperature and pH on equilibrium of biosorption were studied. The experimental data were described with mathematical models, chosen empirically, to assure the highest possible values of determination coefficients, simultaneously with a small number of model parameters. The most commonly used kinetic models incorporate two model parameters: representing the process rate and equilibrium conditions. The process parameters may have an adverse effect on process rate and efficiency. Therefore, it is necessary to choose conditions that favor both kinetics and equilibrium of the process. Models describing equilibrium of biosorption usually incorporate parameters that describe maximum binding capacity of biosorbent and affinity of sorbent to sorbate. Also, in some cases, the process parameters favor on one hand maximum biosorption capacity, but the effect on affinity is adverse. For this reason it is significant to assess the effect of process parameters on process indicators represented by model parameters.

In the present study, a pseudo-second order model was used in the characterization of biosorption kinetics by both wheat straw and grass. The equilibrium of the process performed by wheat straw was described with the Freundlich and by grass by the Langmuir equation. The characterized sorbents possessed intermediate maximum biosorption capacity (ca. 20-25 mg/g). The value is similar to other low-cost sorbents. E.g. for *Sachcharomyces cerevisiae,* maximum sorption capacity for Cu(II) was 10.4 mg/g, for Pb 29.9 mg/g and for Cd 12.8 mg/g [7]. However, the biomass is commonly abundant and of no cost. Therefore, the process efficiency might be improved by increasing the concentration of the sorbent. For this reason, the studied materials have the potential to be applied in wastewater treatment processes. Another issue of concern is further utilization of metal-laden biomass. Wheat straw and grass possess a high heating value (both materials 18 kJ/g) and low ash content (7-9%) [20-21]. Therefore, after combustion of metal-laden biomass it is possible to obtain both, energy and ash being a concentrate of a given metal cation [22]. However, in the combustion of the biomass it would be necessary to treat flue gases and to further utilize the fly ash formed. In the worst case, if it is not possible to recover or to reuse metal it can be utilized by solid waste burial method.

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