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Sorption of cesium from water solutions on potassium nickel hexacyanoferrate-modified *Agaricus bisporus* mushroom biomass

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Abstract In order to gain biosorbent that would have the ability to bind cesium ions from water solution effectively, potassium nickel hexacyanoferrate(II) (KNiFC) was incorporated into the mushroom biomass of *Agaricus bisporus*. Cesium sorption by KNIFC-modified *A. bisporus* biosorbent was observed in batch system, using radiotracer technique using ^{137}Cs radioisotope. Kinetic study showed that the cesium sorption was quite rapid and sorption equilibrium was attained within 1 h. Sorption kinetics of cesium was well described by pseudo-second order kinetics. Sorption equilibrium was the best described by Freundlich isotherm and the distribution coefficient was at interval 7,662–159 cm^3 g^{-1}. Cesium sorption depended on initial pH of solution. Cesium sorption was very low at pH$_0$ 1.0–3.0. At initial pH 11.0, maximum sorption of cesium was found. Negative effect of monovalent (K^+, Na^+, NH_4^+) and divalent (Ca^{2+}, Mg^{2+}) cations on cesium sorption was observed. Desorption experiments showed that 0.1 M potassium chloride is the most suitable desorption agent but the complete desorption of cesium ions from KNiFC-modifed biosorbent was not achieved.

Keywords Cesium · Biosorption · *Agaricus bisporus* · Potassium nickel hexacyanoferrate · Chemical modification

Introduction

From past few decades, considerable efforts have been directed towards the development of various physicochemical methods for removal and recovery of radiocesium from environment involving co-precipitation, coagulation, ion exchange, solvent extraction, electrochemical, and membrane processes [1]. The most frequently used agents for precipitation of Cs radionuclides are transition metal hexacyanoferrates (II, III) which exhibit high sorption selectivity toward these radionuclides and especially that from salinity solutions [2, 3]. The preparation and use of transition metal hexacyanoferrates for the removal of cesium from solution have been studied over the past 50 years [4–12]. However, many ferrocyanides have the form of a fine particle size and are not suitable for column application. For this reason, the preparation of ferrocyanides exchangers has been carried out by precipitation on inert solid supports such as silica gels [13–15], zeolites [16, 17], zirconium hydroxide [2], cellulose, polyacrylonitrile [18], etc. For example, the recovery of ^{137}Cs by sorption from the nitric acid solutions—Purex raffinates—is based upon the application of transition metal ferrocyanide(II)-loaded silicagel of the general formula $K_{1.0}Me^{(II)}_{1.5}Fe^{(II)}(CN_6).nSiO_2$, where $Me^{(II)}$ denotes Ni, Zn, or Cu [19]. However, relatively little is known about the sorption properties of hexacyanoferrates incorporated to different bioorganic supports [1, 20, 21]. It is known, that biomass is able to effectively bind metals and radionuclides from aqueous solutions. This phenomenon is known like a biosorption. On the present, the biosorption is alternative technology for the removal of metals ions and organic pollutants from aqueous solution [22]. During the past 20 years it became obvious that fruiting bodies of higher fungi (mushrooms) are characterized by a high ability to accumulate radionuclides and heavy metals [23–26]. As well, it has been demonstrated that many mushrooms species exhibit high biosorptive potentials [27–31]. Fruit bodies of mushrooms are considered ideal for the purpose of evaluation as biosorbents: they are macro

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in size, tough in texture, and have other physical characteristics conductive for their development as biosorbents [27]. Several chemical processes may be involved in metals biosorption by mushrooms, including adsorption, ion exchange processes, and covalent binding. The polar groups of proteins, amino acids, lipids, and structural polysaccharides (chitin, chitosan, glucans) may take part in biosorption [26]. In the previous works we described of ^{137}Cs uptake by bryophytes and lichens [32–34]. The objective of this study was to investigate the potential of native and chemical modified fruiting bodies of mushroom biomass *A. bisporus* as sorbent for radiocesium from water solution and to obtain quantitative data describing sorption kinetics and equilibrium at different experimental conditions.

Experimental

Reagents

All chemicals used were of pro analysis grade. All working solutions were prepared using of deionized water. Standardized ^{137}Cs solution (5.72 MBq cm^{-3}, 20 mg dm^{-3} CsCl in 3 g dm^{-3} HCl) was obtained from the Czech Institute of Metrology, Prague (Czech Republic).

Preparation of sorbent

The sorbent used in the study were prepared from macro fungi *Agaricus bisporus*. The fresh fruit bodies of *A. bisporus* were purchased from local commercial company. The fruit bodies were cleaned and separated into cap and stipes. Just the caps were used for sorbent preparation. From the caps was removed a skin, the caps were cut into small pieces, and dried in an oven at 60 °C for 24 h. The dried material was extracted in distilled water at 20 °C several times owing to removal of water-soluble compounds. Subsequently, the material was dried in an oven at 60 °C for 24 h. The dried materials were pulverized in a mechanical grinder. The pulverised material was passed through a standard sieves. This material presents a non-modified biosorbent (NB).

NB particles with 150–310 μm size were used for chemical modification. The aim of this modification was incorporated potassium nickel hexacyanoferrates (KNiFC) in the matrix of NB. For this purpose, a procedure of Jalali-Rad et al. [21] was followed. In this procedure, 3 g of NB was added to 100 mL of 0.1 mol dm^{-3} $Ni(NO_3)_2$ solution and shaked at 150 rpm, at 25 °C, for 24 h. After filtration through the filter paper and washing with distilled water, this $NiCl_2$-loaded biosorbent was added to 100 mL of 25 g dm^{-3} potassium hexacyanoferrate(II) solution and left at 25 °C, for 24 h under gentle mixing (shaking at 150 rpm). After 24 h, the KNiFC-loaded biosorbent was separated by filtration, washed with deionized water, and dried at 60 °C for 24 h. This chemical modification biosorbent was used for cesium sorption studies.

Batch sorption experiments

Sorption of Cs on ferrocyanide sorbent or non-modified sorbent (NB) was studied through radioisotope indication using radioisotope of cesium-137. The batch sorption experiments were carried out in 15 cm^3 plastic tubes containing 0.03 g ferrocyanide sorbent or NB sorbent (dry wt.) in 10 cm^3 of cesium chloride solution spiked with ^{137}CsCl (60 kBq dm^{-3}) and adjusted with 0.1 M NaOH to 5.5. The content in tubes was agitated on a reciprocal shaker (120 rpm) at 20 °C. At the end of the experiments, samples were centrifuged at 3,000 rpm for 5 min and the supernatant solutions were analyzed for the residual cesium in the solution by gamma-spectrometry. All experiments were accomplished in duplicate.

The kinetic study was performed with a cesium concentration 200 μmol dm^{-3} for 4 h. The equilibrium study was conducted with the initial cesium concentration varied from 50 to 1,250 μmol dm^{-3} for 2 h. The effect inorganic salts (i.e. NaCl, KCl, NH_4Cl, $CaCl_2$, $MgCl_2$) on cesium sorption was investigated in range 1.10^{-1}–1.10^{-3} mol dm^{-3} at initial CsCl concentration 1.10^{-3} mol dm^{-3}. The influence of initial pH values ranged between 2 and 13 on cesium biosorption was studied. HCl and NaOH were used to adjust the pH (no buffer used).

After cesium sorption (1.0 mmol dm^{-3} CsCl, 60 kBq dm^{-3}, biosorbent 3.0 g dm^{-3}, dry wt., time of sorption 2 h), recovery of cesium from the cesium-loaded sorbent (0.03 g, dry wt.) was examined using 10 mL of deionized water or 10 mL of KCl, NaCl, KOH, NaOH, HCl, and HNO_3 solutions as eluents (0.1 mol dm^{-3}) in batch experiments on a reciprocal shaker (120 rpm) for 30 min at 20 °C.

Radiometric analysis

Radioactivity determination of ^{137}Cs solutions was made with gamma-spectrometric scintillation detector 54BP54/2-X with well type crystal NaI(Tl) (Scionix, NL) with data processing software Scintivision32 (ORTEC, USA). Counting time 600 s allowed obtaining data with measurement error <2%, which do not reflect other source of errors.

Sorption models and statistical analysis

In the present study, various mathematical models were tested for cesium biosorption in batch system in order to obtain comparable and physically interpretable parameters, which describe the sorption process. The model parameters were evaluated by non-linear regression analysis by using OriginPro® 7.0. Nonlinear regression method was based on the Levenberg–Marquardt algorithm, which is the most widely used algorithm in non-linear least squares fitting.

The coefficient of determination (R^2), standard error of the estimate (SEE) and Akaike Information Criterion with a second order correction for small sample sizes ($\mathrm{AIC_C}$) were used to estimate the goodness of the fit of the studied models:

$$R^2 = \frac{\sum_{i=1}^{m} (Y_{i,\mathrm{cal}} - Y)^2}{\sum_{i=1}^{m} (Y_{i,\mathrm{exp}} - Y)^2} \quad (1)$$

$$\mathrm{SEE} = \sqrt{\frac{1}{m-p} \sum_{i=1}^{m} (Y_{i,\mathrm{cal}} - Y_{i,\mathrm{exp}})^2} \quad (2)$$

$$\mathrm{AIC_C} = m \ln\left[\frac{\sum_{i=1}^{m} (Y_{i,\mathrm{cal}} - Y_{i,\mathrm{exp}})^2}{m}\right] + 2(p+1) + 2(p+1)\left(\frac{p+2}{m-p-2}\right) \quad (3)$$

where $Y_{i,\mathrm{cal}}$ is calculated (predicted) i-th value of the dependent variable, $Y_{i,\mathrm{exp}}$ is experimental (observed) i-th value of the dependent variable, Y is the average of all observed values of the dependent variable, m is the number of observations (i.e., number of experimental values), p is the number of parameters in the regression model. A smaller SEE as well as $\mathrm{AIC_C}$ values and a higher R^2 values indicate a better regression model (i.e., a better curve fitting).

Results and discussion

Cesium sorption by non-modified mushroom biosorbent

It is generally known, that cesium is very weak Lewis acid and has a low tendency to interact with ligands. The higher stability constants of cesium (K) were found for crown ether within the range from log K = 3.0 to log K = 5.0, in dependence on the crown ether structure [35]. Preliminary studies showed that the cesium sorption by non-modified *A. bisporus* biomass is lower. At initial cesium concentrations from 10 to 200 μmol dm^{-3}, cesium sorption was in the range 0.1–2.7 μmol g^{-1}, and adsorbed cesium was readily desorbed by deionized water. At initial cesium concentration 200 μmol dm^{-3}, cesium sorption by non-modified biosorbent was 18 times smaller than by KNiFC-modified biosorbent. These results confirmed the fact that cesium ions have the low affinity towards organic ligands such as –COOH, –OH, and –NH$_2$ that are present onto surface of mushrooms biomass. By the aid of FT-IR analysis was found that these functional groups were involved in the biosorption of As(III), As(V) onto macrofungus *Inonotus hispidus* [28] and Pb(II), Cd(II) onto macrofungus *Amanita rubescens* [29]. The only known case of the presence of strong cesium ligands present in mushroom are secondary metabolites (pigments) badione A and norbadione A that were found in the cap skins of *Xerocomus badius* [36, 37]. By reason of lower cesium sorption by non-modified *A. bisporus* biomass, all other sorption experiments have been made by KNiFC-modified *A. bisporus* biosorbent.

Cesium sorption by hexacyanoferrate(II)-modified mushroom biomass

Transition metal hexacyanoferrates (II), also referred to as Prussian blue analogue are known to be highly selective for cesium binding. Prussian blue (PB), i.e., ferric hexacyanoferrate(II) and structurally related compounds under ambient conditions are non-toxic solids, sparingly soluble, and chemically rather inert. The mechanism of cesium binding by PB is not yet known in full detail. Chemical ion exchange, physical adsorption, and ion trapping may all be involved. The primary metal binding mechanism for PB is believed to be the monovalent cesium ion exchange with hydrogen ion ($\mathrm{H^+}$) or from water bound (hydronium ion-$\mathrm{H_3O^+}$) in the PB crystal lattice. Additionally if monovalent cations are present within the lattice as a result of different synthetic reagents and routes, cesium may exchange with alkali metal cation impurities such as sodium or potassium or possibly ammonium [38]. Insoluble hexacyanoferrates exhibit a great variety of compositions and structures. Several compositions may be obtained and different structural arrangements observed with the same transition metal, depending on the method of preparation [5]. Loss-Neskovic et al. [5] showed that the nature of the sorption process strongly depends on the composition and crystal structure of the hexacyanoferrates. The retention of cesium may result from a true ion exchange or may lead to a change of the crystal structure of the solid phase [5, 6, 8]. These different mechanisms result in different sorption kinetics, capacities and stability of the solids, factors that have a significant impact on the choice of the most suitable compounds and experimental conditions for industrial applications [5]. In general, the "zeolite" and "ionic-sieve" effects are typical for an ion-exchange of transition metals on the ferrocyanides [2].In the case of KNiFC, the hypothesis of ion exchange between the potassium ions in the solid and the cesium ions of the solution is generally accepted [5]. On the basis of the works Mimura et al. [17, 39] and Kazemian et al. [16], we suppose that the cesium sorption on the KNiFC-loaded biosorbent can be governed by a cation-exchange reaction

$$K_{2-X}Ni^{II}_{X/2}\left[Ni^{II}Fe^{II}(CN)_6\right] + Cs^+ \leftrightarrow K_{1-X}CsNi^{II}_{X/2}\left[Ni^{II}Fe^{II}(CN)_6\right] + K^+ \quad (4)$$

In order to clarify the mechanism of cesium sorption on the KNiFC-loaded biosorbent, kinetics and isotherm studies, effect of pH and presence of competitive cations on the cesium sorption and elution experiments were done.

Sorption kinetics

Predicting the rate at which the pollutants removal takes place in a given solid/solution system is one of the most crucial factors for the effective sorption system design [40]. Sorption kinetics depends on the interaction between sorbate and sorbent and experimental conditions. In order to clarify the sorption kinetics of Cs ions on hexacyanoferrate(II) modified biosorbent three kinetic models were applied to the experimental data: pseudo-first order model [41] pseudo-second order model [42], and intraparticle diffusion model [43, 44].

The pseudo-first order rate equation is given as

$$q_t = q_e(1 - e^{-k_1 t}) \quad (5)$$

where q_t (μmol g^{-1}) is the amount of cesium adsorbed at any time t (min), q_e (μmol g^{-1}) is the amount of cesium adsorbed at equilibrium, and k_1 (min^{-1}) is the rate constant of sorption. This model assumes that the rate of change of solute uptake with time is directly proportional to difference in equilibrium sorption (q_e) and the amount of solid uptake with time (q_t).

The pseudo-second order rate equation is give as

$$q_t = k_2 q_e^2 t/(1 + k q_e t) \quad (6)$$

where q_t (μmol g^{-1}) is the amount of cesium adsorbed at any time t (min), q_e (μmol g^{-1}) is the amount of cesium adsorbed at equilibrium, and k_2 (g μmol^{-1} min^{-1}) is the rate constant of sorption. The pseudo-second order kinetics is usually associated with the situation when the rate of direct sorption/desorption process (seen as a kind of chemical reaction) controls the overall sorption kinetics [40].

Intraparticle diffusion model is related to time as

$$q_t = k_D t^m \quad (7)$$

where q_t (μmol g^{-1}) is the amount of cesium adsorbed at any time t (min), k_D (μmol g^{-1} min^{-1}) is the rate factor, and m is non-dimensional coefficient which denotes the sorption mechanism. A value of $m = 0.5$ indicates intraparticle diffusion as the rate-determining step.

It was found that the sorption of cesium onto hexacyanoferrate(II) modified biosorbent is a quite rapid process. The most of the cesium was retained within the first minute of contact and that was 38.9 μmol g^{-1}. The experimental equilibrium sorption of cesium was found to be 48.0 μmol g^{-1} at 1 h. The comparable values of cesium sorption were observed in a time interval 1–4 h. A very quick cesium sorption shows a possible ion exchange as one of possible cesium binding mechanisms by hexacyanoferrates (II) [5]. Jalali-Rad et al. [21] observed a very fast cesium sorption by hexacyanoferrate(II)-modified marine algae biomass. They observed that the most of the cesium ions were uptake from solution within 2 min and the equilibrium was established in 30 min. A similar rate of cesium sorption was observed by sorption of radionuclides into mineral adsorbents [45–51].

Figure 1 shows the experimental kinetic data and the curve-fitting plots of the abovementioned three kinetic models. The kinetic parameters obtained by non-linear regression analysis are presented in Table 1 included with statistical parameters. From this table, the comparison of AIC_C, R^2, and SEE values showed that the order of deviation was intraparticle diffusion model > pseudo-first order > pseudo-second order, which indicated that the pseudo-second order model was the best one in describing the adsorption kinetics of cesium on hexacyanoferrate(II) modified biosorbent. This suggests that the pseudo-second order sorption mechanism is predominant and the overall rate of the cesium sorption process appear to be controlled by the chemical process. This supports of hypothesis that chemisorption can have a significant role in cesium binding.

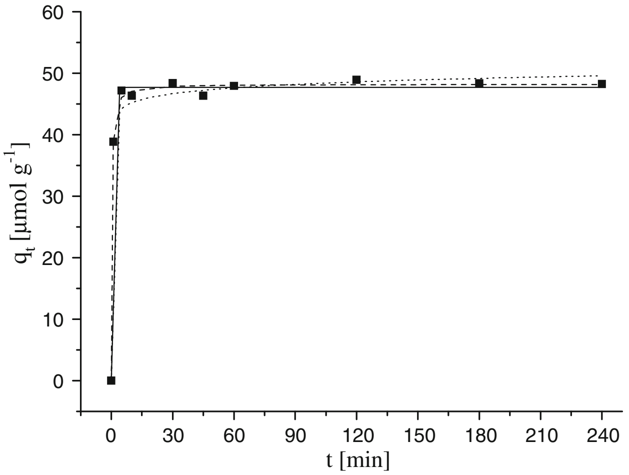

Fig. 1 Comparison of experimental cesium sorption kinetics (*black points*) against theoretical predictions based on the pseudo-first order kinetics (*solid line*), pseudo-second order kinetics (*dashed line*), and on the diffusion kinetic model (*dotted line*). Experimental conditions: initial cesium concentration 200 μmol dm^{-3}, solid/liquid ratio 3.0 g dm^{-3}, pH_0 5.5, temperature 20 °C. Each point is the arithmetic mean of two data

Table 1 Kinetic model parameters of cesium sorption by KNiFC-modified *A. bisporus* biomass obtained by using non-linear regression analysis and their statistical characteristics

Kinetic model	Parameter ± SE	R^2	SEE	AIC_C
Pseudo-first-order	$q_e = 47.7 \pm 0.4$	0.9997	0.916	6.02
	$k_1 = 1.68 \pm 0.11$			
Pseudo-second-order	$q_e = 48.2 \pm 0.4$	0.9997	0.836	4.18
	$k_2 = 0.09 \pm 0.01$			
Intraparticle diffusion	$k_D = 42.2 \pm 1.4$	0.9982	1.867	20.3
	$m = 0.029 \pm 0.008$			

SE standard error on parameter value, R^2 the coefficient of determination, *SEE* standard error of the estimate, AIC_C Akaike Information Criterion

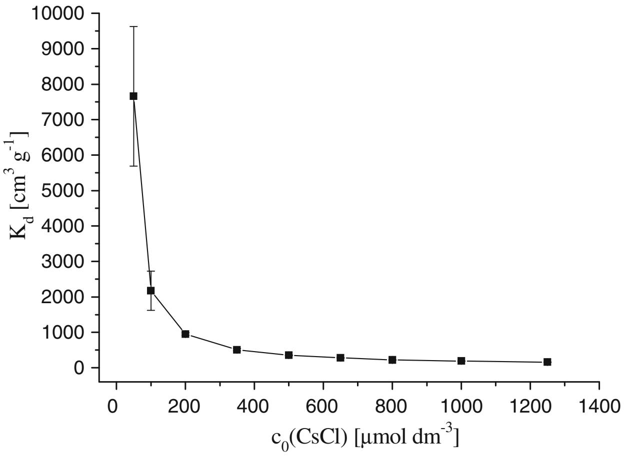

Fig. 2 Distribution coefficient of cesium as a function of initial CsCl concentration in the range 50–1,250 μmol dm^{-3}, solid/liquid ratio 3.0 g dm^{-3}, pH$_0$ 5.5, temperature 20 °C. Each point is the arithmetic mean of two data and *error bars* represent standard deviation of the mean

Sorption equilibrium

The sorption of cesium onto hexacyanoferrate(II) modified biosorbent was studied in the concentration range 0.05–1.25 mmol dm^{-3}. The maximum cesium uptake was found to be 135 μmol g^{-1} at initial CsCl concentration 1.25 mmol dm^{-3}. The distribution coefficient of Cs (K_d) as a function of initial CsCl concentration is presented in Fig. 2. The values of the K_d were at intervals 7,662–159 cm^3 g^{-1}. The highest value of K_d was observed in the lowest concentration of Cs in solution (i.e., at 0.05 mmol dm^{-3}). Subsequently, the strong decrease of distribution coefficient with the increasing concentration CsCl has been observed. This drastic decrease of the K_d in the case of higher concentration of cesium is causing a decrease of the sorption capacity by cesium occupying of sorption site of sorbents [15].

Equilibrium data, known as sorption isotherms, reveal the specific relation between the concentration of adsorbate and its sorption degree onto adsorbent surface at a constant temperature. In this study, the equilibrium experimental data for cesium sorption on hexacyanoferrate modified biosorbent were analyzed using the Langmuir [52] and Freundlich isotherm [53].

The Langmuir model assumes monolayer adsorption (the adsorbed layer is one molecule in thickness), with adsorption can only occur at a finite (fixed) number of definite localized sites, that are identical and equivalent, with no lateral interaction and steric hindrance between the adsorbed molecules, even on adjacent sites. The Langmuir equation can be written as follows

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e} \tag{8}$$

where C_e (μmol dm^{-3}) and q_e (μmol g^{-1}) are the liquid phase concentration and solid phase concentration of adsorbate at equilibrium, respectively; $q_{\max}$ (μmol g^{-1}) is the monolayer adsorption capacity of the adsorbent and b (μmol dm^{-3}) is Langmuir adsorption constant which related with free energy of adsorption and it is attributed to the affinity between the adsorbent and adsorbate.

The Freundlich model assumes non-ideal sorption on heterogeneous surfaces and multilayer sorption with interaction between adsorbed molecules. The Freundlich equation is give as

$$q_e = K_F C_e^{1/n_F} \tag{9}$$

where K_F (dm^3 μmol^{-1}) is constant related to the adsorption capacity which represents the affinity between the sorbate and the sorbent and $1/n_F$ (non dimensional) is an empirical parameter related to the adsorption intensity, which varies with the heterogeneity of the adsorbent. The value of $1/n_F$ ranges between 0 and 1, and indicates the degree of non-linearity between solution concentration and adsorption as follows: if the value $1/n_F$ is equal to unity, the adsorption is linear; if the value is below unity, this implies that the adsorption process is chemical; if the value is above unity, adsorption is a favorable physical process; the more heterogeneous the surface, the closer $1/n_F$ value is to 0. The case $1/n_F < 1$ reflects the situation in which at higher and higher adsorbate concentrations, it becomes more and more difficult to adsorb additional molecules. This may occur in cases where specific binding sites become filled or remaining sites are less attractive to the adsorbate molecules or ions.

The experimental isotherm with the fitted curves is depicted in Fig. 3 and the isotherm parameters are presented in Table 2. It can already be seen from the graphical evaluation that the Freundlich model gives the best fit, which is confirmed by the AIC_C, R^2, and SEE values. The

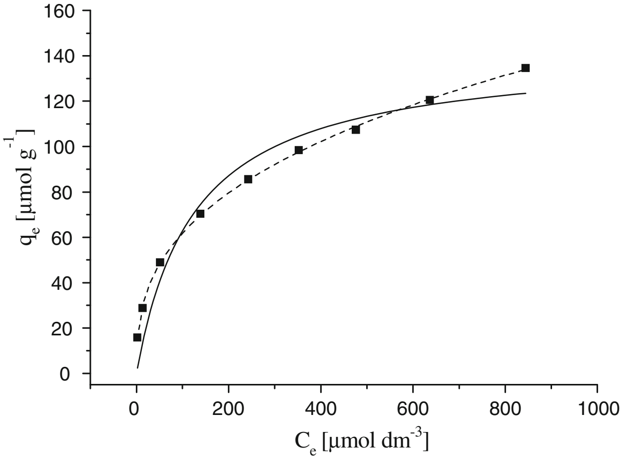

Fig. 3 Comparison of experimental cesium sorption isotherm (*black points*) against theoretical predictions based on the Langmuir model (*solid line*) and Freundlich model (*dashed line*); initial cesium concentrations were in the range 50–1,250 μmol dm^{-3}, solid/liquid ratio 3.0 g dm^{-3}, pH$_0$ 5.5, temperature 20 °C. Each point is the arithmetic mean of two data

Table 2 Isotherm model parameters of cesium sorption by KNiFC-modified *A. bisporus* biomass obtained by using non-linear regression analysis and their statistical characteristics

Isotherm model	Parameter ± SE	R^2	SEE	AIC$_C$
Langmuir	$q_{max} = 142 \pm 12$ $b = 0.008 \pm 0.002$	0.9460	10.21	50.4
Freundlich	$K_F = 11.7 \pm 0.3$ $n_F = 2.76 \pm 0.03$	0.9996	0.927	7.18

SE standard error on parameter value, R^2 the coefficient of determination, *SEE* standard error of the estimate, *AIC*$_C$ Akaike Information Criterion

values of the Freundlich constants K_F and n_F were found to be 11.7 and 2.76. Rajec et al. [14] reported that cesium sorption onto potassium nickel hexacyanoferrates incorporated in silica gel matrix was described by Langmuir isotherm and a calculated capacity was found in the range 0.13–0.41 mmol g^{-1}. Milonjić et al. [13] obtained similar results at cesium sorption onto copper hexacyanoferrate/polymer/silica sorbents and the calculated capacity was 0.15 mmol g^{-1}. Jalali-Rad et al. [21] reported that a sorption by hexacyanoferrate(II)-modified marine algae biomass was described by Langmuir isotherm rather than Freundlich isotherm. As well, they found that the cesium sorption capacity for native marine algae was in the range 0.11–0.54 mmol g^{-1} and for modified marine algae was in the range 0.18–1.50 mmol g^{-1}. In our case, the cesium sorption by KNiFC-modified mushroom biomass was described by Freundlich isotherm better than by Langmuir isotherm. This fact implies the chemisorption on the heterogeneous surface. Generally, the surface heterogeneity stems from two sources known as geometrical and chemical ones. Geometrical heterogeneity is a result of differences in size and shape of pores, cracks, pits, and steps. Chemical heterogeneity is associated with different functional groups or different affinity sites that are present on the surface of sorbent [54]. Both chemical and geometrical heterogeneities can contribute to the sorption of cesium ions on KNiFC-modified mushroom biomass.

Effect of pH

The solution pH is a crucial factor in metals sorption. The pH value significantly influences the dissociation site on the surface of the biosorbent and the solution chemistry of the metals, e.g., hydrolysis, complexation by organic and/or inorganic ligands, redox reactions, and precipitation, as well as the speciation and sorption availability for metals [22].

It is known that transition metal hexacyanoferrates are able to effectively bind cesium in acidic (in the presence of 0.1 M HNO$_3$) and in alkaline pH (pH ~ 8–11). In this study, the effect pH on cesium sorption onto KNiFC-loaded biosorbent was studied in the range 1.0–13.0. Figure 4 shows the dependence of the distribution coefficient of cesium on initial pH of cesium solution. It can be seen that the dependence of K_d value on pH exhibits two maxima and that at pH 5.0 (less) and pH 11.0 (larger). Valsala et al. [55] reported a similar pH-dependency of cesium sorption onto cobalt ferrocyanide impregnated anion exchange resin. They observed two sorption maximums, at pH 4.0 and 9.0. However, they observed that the cesium sorption at pH 4.0 was higher than at pH 9.0.

Cesium sorption onto KNiFC-loaded biosorbent was very low in interval from pH 1 ($K_d = 42.0$ cm^3 g^{-1}) to 3 ($K_d = 50.0$ cm^3 g^{-1}), what shows a significant competition of H$^+$ ions with cesium ions for the same sites binding of sorbent if we presume, that ion exchange is the main mechanism of cesium sorption. Also by influence of low pH solution, it could come to destruction of sorbent, what would lead also to decrease of sorption capacity of sorbent. Mimura et al. [39] and Ismail et al. [11] confirmed of K$^+$/H$^+$ ion exchange within the hexacyanoferrates structure in the presence of nitric acid. Mimura et al. [2] simultaneously observed the Fe(II) oxidation of KNiFC on Fe(III). Generally, they observed that the concentration of H$^+$ ions up to 1.0 mol dm^{-3} had a small effect on cesium uptake by KNiFC.

It is known, that the metal cations are characterized by very low biosorption in the pH range of 1–2, as confirmed in our previous works [56–58]. At pH 3.0–4.0, a significant increase in the sorption of metal cations occurs. That is associated with a reduction in the concentration of H$^+$ ions which compete with metal cations for the same binding

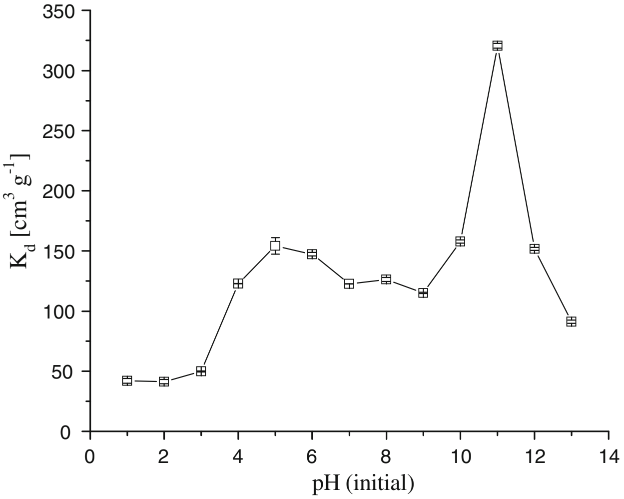

Fig. 4 Distribution coefficient of cesium as a function initial pH, initial cesium concentration 1.0 mmol dm^{-3}, solid/liquid ratio 3.0 g dm^{-3}, pH$_0$ 5.5, contact time 2 h, and temperature 20 °C. Each point is the arithmetic mean of two data and *error bars* represent standard deviation of the mean

sites on the surface of sorbent. Also, by reducing the concentration of H^+ ions, the surface deprotonization of biosorbent occurs, which results into increase in the number of effective sorption sites on the surface of biosorbent. With further increase in pH, sorption of metal cations usually further increases. Higher pH (pH >6) values could not be applied because of the formation of metal hydroxide (i.e., precipitates). However, it is known that a cesium is in the form of free Cs^+ ions in the alkaline pH. On the basis of these facts we assume that in the pH range of 1.0–9.0, cesium sorption is significantly influenced by support properties. With further increase in pH in the range of 9.0–11.0, cesium sorption increased, while at pH 11.0, K_d value reached second maximum. As shown in Fig. 4, at pH 11.0, the K_d had twice greater value than at pH 5.0. With a further increase in pH, K_d drastically decrease. The works of Milyutin et al. [3, 4] and Sharygin et al. [2] confirmed the fact that nickel and copper ferrocyanides showed enhanced the ability of cesium uptake in alkaline solutions. Primarily, it is in the pH range 8.0–10.0. This fact relates with the increased stability of ferrocyanides in alkaline solutions. However, the cesium sorption of the ferrocyanide sorbents drastically decreases at pH >11.0 because of dissolution of the ferrocyanide component of the sorbent. This fact was confirmed by Milyutin et al. [3] who observed a sharp increase of free $Fe(CN)_6^{4-}$ ions in the strong alkaline solution owing to the reaction of OH^- ions with the precipitate of the copper ferrocyanide. Mimura et al. [59] observed that the structure of KNiFC was destroyed by treatment with NaOH above 1 M, due to the hydrolysis of the constitutional element of Ni and the release of iron as $Fe(CN)_6^{4-}$ ions which led to a considerable lowering of the cesium ions uptake ability.

The effect of competitive ions

The effect of monovalent (Na^+, K^+, $NH_4{}^+$) and divalent (Ca^{2+}, Mg^{2+}) cations on K_d of cesium was examined. The distribution coefficient of cesium ions as a function of competitive ions concentration is presented in Fig. 5. It can be seen that the K_d values of cesium increase when initial concentration of competitive solution cations decreases. The highest values of K_d were attained at the lowest concentration of ions 1.0 mmol dm^{-3}. The sorption of cesium ions strongly depends on initial concentration of competitive monovalent cations. At the initial concentrations of monovalent cations 10 and 100 mmol dm^{-3}, the increasing competitive effect of the cations on the cesium K_d is as follows: $Na^+ < K^+ < NH_4{}^+$. This rating of the selectivity of the cations of alkaline metals and ammonium is typical for nickel ferrocyanide [2] but also clays [45]. In general, monovalent alkali metals are bound with increasing strength in the following order $Na^+ < K^+ < NH_4{}^+ < Rb^+ < Cs^+$, according to their increasing ionic radii [6]. At the initial concentrations 1 mmol dm^{-3}, it was observed the similar influence of all monovalent cations on the cesium sorption ($K_d \sim 120$ cm^3 g^{-1}). When comparing the effect of the competitive monovalent and bivalent cations at initial concentration 100 mmol dm^{-3}, it can be seen that the ability of the cations to depress the sorption of cesium follow the order $NH_4{}^+ > K^+ > Ca^{2+} > Mg^{2+} > Na^+$. The strong

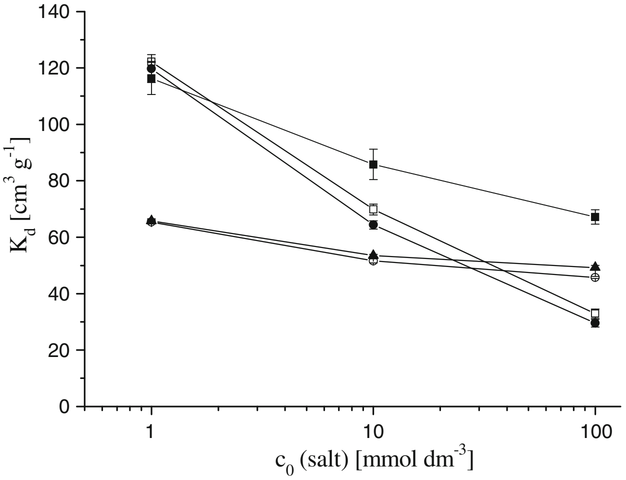

Fig. 5 Distribution coefficient of cesium as a function of competitive ions concentration in semi-logarithmic scale: *filled square* Na^+, *open square* K^+, *filled circle* $NH_4{}^+$, *open circle* Ca, and *triangle* Mg. The K_d value without addition of salts was 189 ± 8 cm^3 g^{-1}. Experimental conditions: initial cesium concentration 1.0 mmol dm^{-3}; solid/liquid ratio 3.0 g dm^{-3}, pH$_0$ 5.5, contact time 2 h, and temperature 20 °C. Each point is the arithmetic mean of two data and *error bars* represent standard deviation of the mean

influence of potassium and ammonium ions on sorption of cesium ions suggesting that the uptake of Cs^+ ions on hexacyanoferrate(II) modified biosorbent could be governed by a cation-exchange reaction of $K^+ \leftrightarrow Cs^+$ [39]. However, at the initial concentrations of competitive cations 1 and 10 mmol dm^{-3}, the K_d value was lower in the presence of divalent cations than in the presence of monovalent cations. It can be seen that divalent cations had pronounced competitive effect on cesium uptake at initial concentration 1 mmol dm^{-3}. It is known that divalent ions have more contribution to ionic strength and more positive charge than monovalent cations. For these reasons, the effect of divalent cations Ca^{2+} and Mg^{2+} on cesium sorption is more serious than monovalent ions. However, it is generally believed that insoluble hexacyanoferrates(II) and (III) have little affinity for alkaline-earth ions. It was found that these ions were retained with a decreasing affinity according to the order: Ba > Sr > Ca > Mg [60]. In general, we can say that the influence of cations on cesium sorption could be caused by competitive ion exchangeable reactions and by occupying of active sorption centres of KNiFC-modified biosorbent.

Desorption of ^{137}Cs

For the desorption experiments, several solvents (acids, alkali, salts, and deionized water) have been used. Batch desorption experiments were carried out and desorption efficiencies are compared in Fig. 6. It can be seen that the efficiency of desorption agents declines in the order (in parentheses are presented the percentage desorption): KCl (81.0%) > KOH (73.3%) > HNO_3 (70.9%) > HCl (69.7%) > NaCl (64.3%) > NaOH (55.2%) > $H_2$0 (6.4%). In comparison with others agents, it is clear that the cesium desorption by deionized water is very low which may be caused by the strong interaction between cesium ions and KNiFC-modified biosorbent. It can be seen that the ability of cations to desorb of cesium ions dropped in the order: $K^+ > H^+ > Na^+$. The cesium desorption was best achieved using potassium chloride which implies that the cesium binding by KNiFC-modified biosorbent can be governed by a cation-exchange reaction of $K^+ \leftrightarrow Cs^+$.

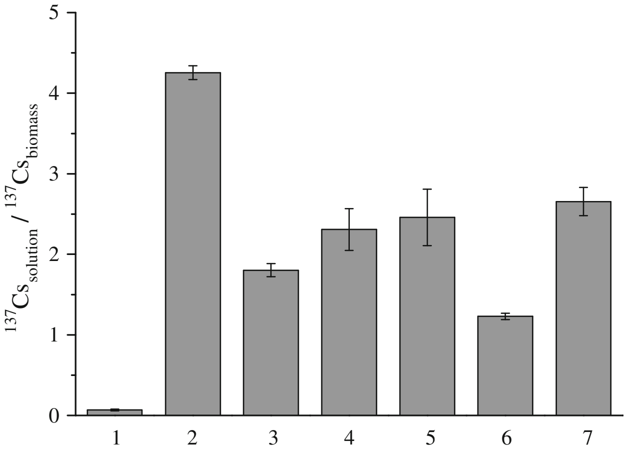

Fig. 6 Desorption of cesium-137 from ^{137}Cs-loaded biosorbent using various extraction agents (*1* $H_2$0, *2* 0.1 M KCl, *3* 0.1 M NaCl, *4* 0.1 M HCl, *5* 0.1 M HNO_3, *6* 0.1 M NaOH, and *7* 0.1 M KOH)

In general, the efficiency of desorption ranged from 6.4 to 81.0% which means that the complete desorption of cesium ions was not achieved. We assume that the residual cesium (i.e., cesium non-desorbed by 0.1 M KCl) could be bound by other mechanism than is true ion-exchange between K^+ and Cs^+ ions. For example, cesium can be bound still unknown electrostatic interaction or cesium could be entrapment in cavities that could be created during biosorbent modification by KNiFC. Sharygin et al. [2] investigated the sorption of cesium on nickel ferrocyanide disperses in the zirconium hydroxide (TERMOXID®, Russia). They carried out adsorption and desorption isotherm and they observed sorption–desorption hysteresis which pointed to that cesium sorption on the Termoxid is irreversible. For reason given, the spent Termoxid is not recoverable and must be sent for burial as solid radioactive wastes. Gelis et al. [19] mentioned that desorption of the sorbed cesium by transition metal ferrocyanides incorporated into silica gel can be achieved by oxidation of the $Fe(CN_6)$ groups (i.e., by oxidation Fe^{II} to Fe^{III}). Subsequently, regeneration of the sorbent is achieved by treating the oxidized sorbent form with the solution of a reductant in the presence of potassium ions.

Conclusions

For the purpose of potassium nickel hexacyanoferrate (KNiFC)-loaded biosorbent preparation, the *Agaricus bisporus* biomass was modified by successive impregnation of $Ni(NO_3)_2$ and $K_4Fe(CN)_6$. Presented study showed that in comparison with non-modified *A. bisporus* biomass, KNiFC-modified biomass was able to bind cesium ions from water solution. However, sorption of cesium by KNiFC-modified mushroom biomass was less selective and it was affected significantly by the present of competitive inorganic cations. On the other hand, the ubiquity of mushrooms and their availability, their relatively low price and eco-friendliness makes them alternative support of transition metal hexacyanoferrates.

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