Journal of Hazardous Materials B121 (2005) 167–173

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Biosorption of Cr(III) ions by eggshells

Katarzyna Chojnacka *

Institute of Chemical Engineering and Heating Equipment, Wroclaw University of Technology, ul. Norwida 4/6, 50-373 Wroclaw, Poland

Received 25 November 2004; received in revised form 9 February 2005; accepted 10 February 2005
Available online 13 March 2005

Abstract

The paper presents results of studies carried out on sorption of Cr(III) ions from aqueous solutions by eggshells as a low-cost sorbent. It was found that crushed eggshells posses relatively high sorption capacity, when comparing with other sorbents, that was evaluated as 21–160 mg/g. The effect of process parameters: pH, temperature, initial concentration of Cr(III) ions on the process kinetics was studied. It was found that the equilibrium of the process was reached after 60 min. Also equilibrium studies were performed: the effect of sorbent concentration and equilibrium Cr(III) concentration was studied. The maximum experimentally determined sorption capacity 160 mg/g was obtained at low sorbent concentration at 20 °C and pH 5. It was found that sorption capacity increased with the increase of Cr(III) concentration, temperature and sorbent concentration. Mathematical models describing kinetics and equilibrium of sorption were proposed. The process kinetics was described with pseudo-second-order pattern and equilibrium was described with Langmuir-type equation, and the influence of sorbate concentration, with an empirical dependence. The models were positively verified. Eggshells were able to remove the concentration of Cr(III) ions below the acceptable level, i.e. at 40 °C, at the initial concentration of metal ions 100 mg/kg, at sorbent concentration 15 g/l.

Keywords: Sorption; Eggshells; Modelling; Kinetics; Equilibrium

1. Introduction

The source of environmental pollution with heavy metals is mainly industry, i.e. metallurgical, electroplating, metal finishing industries, tanneries, chemical manufacturing, mine drainage and battery manufacturing [1]. Recently, heavy metal ions removal from industrial waste streams became particularly difficult due to implementation of more restrict law regulations that control the concentration of pollutants in effluents discharged into waters and soil on the level lower than 1 mg/kg. Traditional methods of metal ions removal became inefficient in the removal of metal ions below this concentration. Therefore, there is the need to search for other methods that would be efficient at low concentration of pollutants. Such a possibility offers a method that uses sorbents of biological origin [2–4] for the removal of toxic metals from dilute aqueous solutions [1]. The most frequently studied biosorbents are bacteria [5], fungi [6] and algae [7]. But more recently, biological sorbents are searched among waste materials from food and agricultural industry. These materials can be considered as low-cost sorbents [8]. Bailey et al. [2] reported the characteristics of low-cost sorbents: it should require little processing, should be abundant in nature or should be a by-product or waste material from another industry. Low-cost sorbents cited by the authors include: bark, lignin, chitin, seaweed, zeolite, clay, fly ash, peat moss, exhausted coffee, waste tea, orange peel, animal bones [9]. Williams et al. [10] reported waste materials, including agricultural products: wool, rice, straw, coconut husks to be used as low-cost sorbents. If low-cost sorbents are used in wastewater treatment process, the process cost would be significantly reduced [11].

In the present paper it is proposed to apply hen eggshells as low-cost biological sorbent of metal ions. In USA annually 120,000 tones of waste eggshells is generated and disposed in landfills [12]. The eggshell (which is almost entirely disposed of as waste) is currently used as a source of calcium in animal feeds and human health supplements (i.e. for osteoporosis) [13].

* Tel.: +48 71 3203131; fax: +48 71 3203469.
E-mail address: k.chojnacka@ch.pwr.wroc.pl.

0304-3894/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2005.02.004

Nomenclature

b	Langmuir sorption constant (kg/mg)
C_{eq}	residual metal ion concentration at equilibrium (mg/kg)
C_S	eggshells concentration (g/l)
C_0	initial metal ion concentration (mg/kg)
d	model parameter (Eq. (4)), sorbent concentration at which $0.5q_m$ is reached (g/l)
k	pseudo-second-order sorption rate constant (g/(mg min))
q	sorption capacity (mg/g)
q_{eq}	sorption capacity at equilibrium (mg/g)
q_m	Langmuir sorption constant (mg/g)
R^2	regression coefficient
T	solution temperature (°C)

About 85–95% of the dry eggshell is calcium carbonate, 1.4% magnesium carbonate, 0.76% phosphates, 4% organic matter [14]. Eggshell contains also traces of sodium, potassium, zinc, manganese, iron and copper [15]. If calcium from the shell is removed, the organic material is left that possesses calcium (or other metal cation) binding properties [16]. Since eggshell is composed mainly of calcium carbonate, it should behave as known sorbents that contain this compound, i.e. calcite [17], calcareous soil [18]. Therefore, sorption by eggshells should occur mainly via exchange reaction and it should be possible to use it as a new biological sorbent of metal ions.

The fundamental characteristics of a new biological sorbent should include investigation of kinetics and statics of sorption process. The study of sorption kinetics in wastewater treatment is significant as it provides valuable insights into the process mechanism. It is important to be able to predict the rate at which pollutant is removed from waste aqueous solutions [19]. Equally important is to study the process equilibrium. The equilibrium of sorbate distribution between the sorbent and solution is important in determining the maximum sorption capacity. Both, kinetics and statics of the process should be described with simple, mathematical models to predict the efficiency of the process and to design wastewater treatment unit.

In the present work, a new biological sorbent – eggshells – was characterized and used in sorption of Cr(III) ions (as example cations) from aqueous solutions. Chromium(III) is an essential element, but its elevated concentrations in the environment are hazardous to fauna and flora [20]. The following industries cause environmental emissions of chromium(III): stainless steel production, leather tanning, metal plating, chemicals production. In Poland, pollution with Cr(III) is of particular concern. The effect of process parameters, such as the concentration of Cr(III) ions and initial pH, temperature, biomass concentration, on process kinetics and the effect of sorbent concentration, initial pH, and temperature on process equilibrium were studied. Mathematical models describing kinetics and statics of sorption were proposed.

2. Materials and methods

2.1. Sorbent preparation

Hen eggshells were collected from eggs from a grocery shop. The eggshells were washed with tap water for several times and afterwards with redistilled water for three times. Then, they were transferred to the oven at 80 °C to dry. The dried eggshells were crushed and milled. The average size of eggshells was 100 μm. No storage problems were observed.

2.2. Batch sorption experiments

The experiments were performed in 250 ml Erlenmeyer flasks containing 100 ml of solution of chromium(III) ($Cr(NO_3)_3·9H_2O$ from POCh Gliwice S.A., Poland) in thermostated water bath shaker at 150 rpm. pH of the solution was adjusted with 0.1 mol/dm^3 solution NaOH, with the precision of ±0.05. The temperature was controlled with the precision ±1 °C. In equilibrium experiments, the contact time was evaluated from kinetic experiments as 120 min. Samples of sorbent suspension (5 ml) were taken to determine residual concentration of chromium(III) in the solution. Before analysis, samples were immediately filtered through No. 2 paper filter.

The concentration of chromium(III) ions in the samples was determined by Inductively Coupled Plasma Spectrometry ICP-AES plasma spectrometer (Philips Scientific PU 7000). pH measurements were conducted with Mettler Toledo MA235 pH/ion analyzer. The samples were analyzed in three repeats (the relative standard deviation of the measurement did not differ from the acceptable for Certified Reference Materials).

3. Results and discussion

The mechanism of sorption by eggshells has not been studied in the literature. However, basing on studies performed for other sorbents of animal origin, i.e. animal bones [9] the process should depend on pH and temperature. Therefore, in the present work, the sorption of Cr(III) ions to eggshells was investigated as a function of initial pH, temperature, and initial Cr(III) concentration.

3.1. Kinetic modelling

Mathematical models that are used the most frequently to describe kinetics of sorption in a free suspension in a well-agitated batch system (so the effect of external film diffusion on the process rate can be ignored) are pseudo first- and

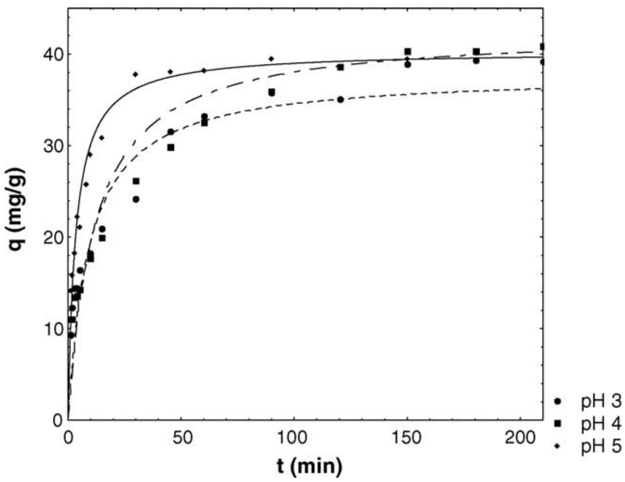

Fig. 1. The effect of pH on sorption kinetics (C_0 200 mg/kg, 20 °C, C_S 5 g/l).

second-order equations, after the assumption that measured metal concentrations are equal to cell surface concentrations [21]. Pseudo-second-order rate model is based on the assumption that chemical sorption involving valency forces through sharing or exchange of electrons between sorbent and sorbate is the rate limiting step [19].

The experimental data of the process kinetics were fitted to first, pseudo first- and pseudo-second-order kinetic equation. The highest average regression coefficients ($R^2 > 0.995$) were obtained for pseudo-second-order kinetic equation (Eq. (1))

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

and this model was further used to describe the process rate. Model parameters (determined by linearization) for kinetic experiments performed at different process parameters: pH (3–5) (Fig. 1), temperature (20–60 °C) (Fig. 2) and C_0 (100–300 mg/kg) (Fig. 3) are presented in Tables 1–3.

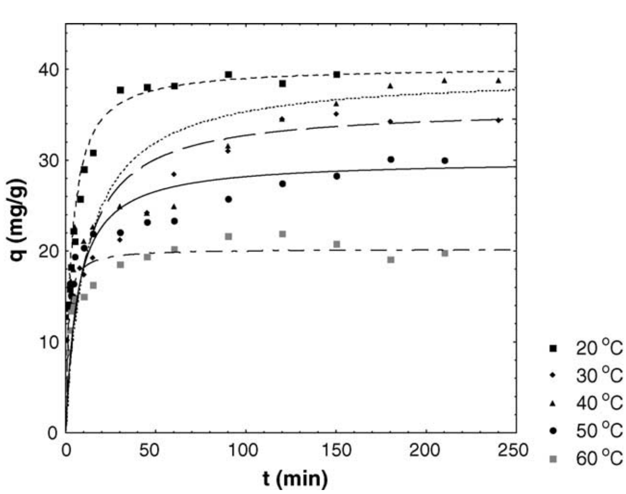

Fig. 2. The effect of temperature on sorption kinetics (C_0 200 mg/kg, pH 5, C_S 5 g/l).

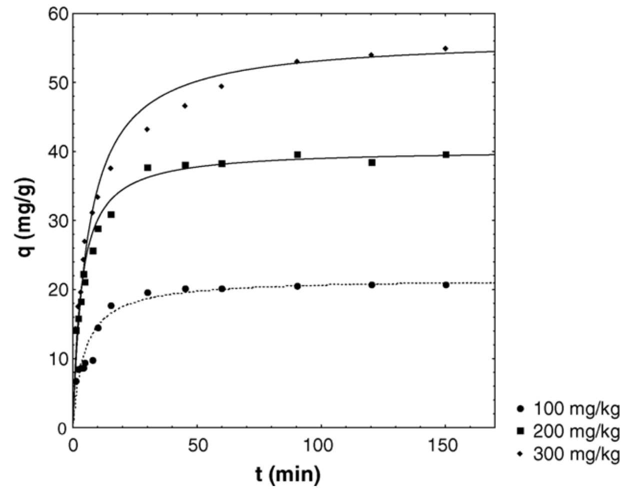

Fig. 3. The effect of initial concentration of Cr(III) ions in the solution on sorption kinetics (20 °C, pH 5, C_S 5 g/l).

Table 1
A comparison of second-order sorption rate constants at different pH (C_0 200 mg/kg, T 20 °C, C_S 5.0 g/l)

pH	q_{eq} (mg/g)	k (g/(mg min))	R^2
3	37.84	0.002810	0.9947
4	42.55	0.001988	0.9945
5	40.32	0.007300	0.9994

Table 2
A comparison of second-order sorption rate constants at different temperatures (C_0 200 mg/kg, pH 5.0, C_S 5.0 g/l)

Temperature (°C)	q_{eq} (mg/g)	k (g/(mg min))	R^2
20	40.32	0.007300	0.9994
30	35.84	0.002935	0.9936
40	39.53	0.002139	0.9854
50	30.03	0.005094	0.9935
60	20.24	0.04327	0.9958

3.1.1. Effect of initial pH

pH is an important process parameter in sorption, since it is responsible for protonation of metal binding sites, calcium carbonate solubility and metal speciation in the solution. It was found that Cr(III) uptake by eggshells was a function of solution pH. The effect of pH was studied at 20 °C at initial Cr(III) concentration 200 mg/kg (Fig. 1, Table 1). The increase of pH resulted in increase of k.

The rate of sorption at pH 5 was significantly higher than at pH 3 and 4. The equilibrium sorption capacity was similar at pH 4 and 5 and was lower at pH 3. This means that when considering biosorption kinetics and equilibrium, it is the

Table 3
A comparison of second-order sorption rate constants at different initial Cr(III) concentration (T 20 °C, pH 5.0, C_S 5.0 g/l)

C_0 (mg/kg)	q_{eq} (mg/g)	k (g/(mg min))	R^2
100	21.60	0.009950	0.9986
200	40.32	0.007300	0.9994
300	56.50	0.002807	0.9985

Table 4
A comparison of the model sorption constants obtained for the equilibrium model proposed at different temperatures and pH (C_S 1–15 g/l, C_0 100–300 mg/kg)

Temperature (°C)	pH	q experimental at C_S = 1 g/l	q_m (mg/g)	b (kg/mg)	d (g/l)	R^2
20	5	159.9	502.8	0.3095	0.04914	0.9921
30	5	25.6	142.0	0.01220	0.4645	0.8931
40	5	57.3	110.7	0.01030	0.6815	0.8912
50	5	72.5	77.78	0.02010	1.583	0.8292
60	5	66.2	153.3	0.4010	0.5565	0.9090
22	3	21	22.72	0.09648	1.421	0.7766
60	3	29.4	22.15	0.3612	13.016	0.9410

mostly advantageous to carry out biosorption at pH 5. The effect of pH can be explained by ion-exchange mechanism of sorption in which the important role is played by carbonate groups that have cation-exchange properties. At lower pH, protons compete with metal ions for a binding site. At lower pH, the concentration of protons is higher, and thus more groups are bound with protons and therefore less groups is available to metal ions.

In this study co-effect of pH and temperature was observed. The strongest influence of temperature was observed at pH 5 than at pH 3 (Tables 1 and 4). At pH 3 biosorption capacity was significantly lower than at pH 5. By considering the mechanism of the process, including Cr(III) ions binding to carbonate sites and the influence of pH on metal chemistry in the solution, at pH 3 the majority of sites were bound with protons and were thus were not available to metal ions. This effect was stronger than the effect of temperature.

3.1.2. Effect of temperature

The effect of temperature (Fig. 2, Table 2) was studied in the temperature range 20–60 °C at pH 5, C_S 5 g/l, C_0 200 mg/kg. It was found that q_{eq} decreased with increase of temperature, which was probably related with increased solubility of chromium carbonate at higher temperatures. Eggshells are composed mainly of calcium carbonate, with some contribution of organic matter. Generally, carbonates and organic matter constitute the skeleton of eggshells. Calcium ions are bound via ion-exchange and can be thus exchanged by other cations – in this case chromium ions. In some cases, it is possible that chromium carbonate precipitates on the surface of eggshells. At elevated temperature, the solubility of chromium increases, and thus biosorption capacity of eggshells decreases. The value of sorption rate constant slightly decreased between 20–40 °C and above 40 °C increased. The increase was significant between 50 and 60 °C. This could be explained by dramatic changes in the nature of the sorbent (i.e. denaturation of protein) at this temperature

3.1.3. Effect of initial Cr(III) concentration

In Fig. 3 there is shown the effect of initial concentration of Cr(III) ions on process kinetics. The data presented are for 20 °C, pH 5, C_S 5 g/l and were described with the model equation (Eq. (1), Table 3). It was found that with the increase of initial Cr(III) concentration, q_{eq} increased and k decreased linearly. Increase of q_{eq} with the increase of C_0 was as expected (it was confirmed by equilibrium studies – isotherms), due to the increase of sorption surface area, whereas the sorbed Cr(III) ions quantity per unit weight of eggshells (q) decreased by increasing eggshells quantity. It was found, that increasing the initial sorbate concentration resulted in decrease of the rate of sorbate sorption. At increased metal ions concentration in the solution, the diffusion of Cr(III) ions in the boundary layer and thus resulted in slower diffusion in eggshell. At low initial metal ions concentration, sorption occurred faster due to larger difference in concentration between eggshells surface and the boundary layer or a strong driving force.

3.2. Equilibrium modelling

The most frequently used sorption equilibrium models (isotherms) are Langmuir and Freundlich equations. In the case of eggshells, however it was found that models describing sorption uptake as the function of only chromium concentration were not suitable, since it was found that the process equilibrium strongly depended on sorbent concentration (Figs. 4 and 5) that had an impact on pH, solubility

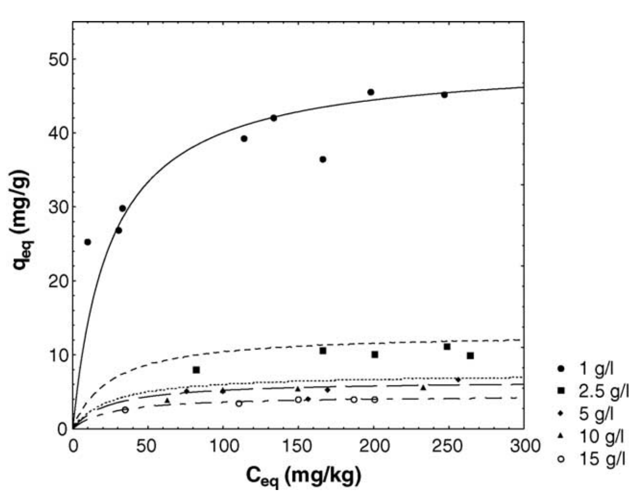

Fig. 4. Isotherms carried out for various sorbent concentrations at 20 °C, pH 5.

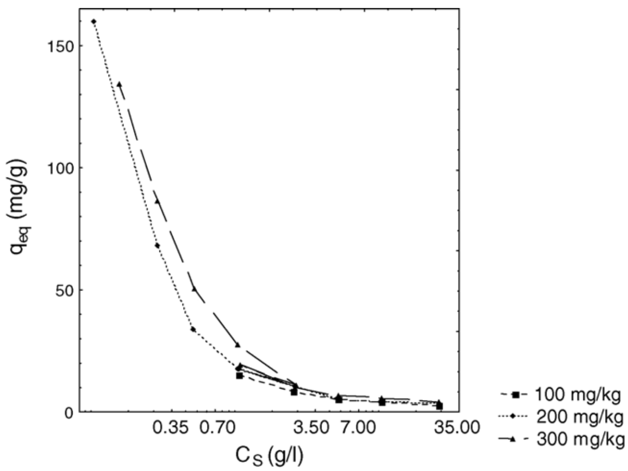

Fig. 5. The effect of initial Cr(III) concentration on biosorption capacity at various sorbent concentrations at 20 °C, pH 5.

of carbonates etc., since eggshells are composed mainly of calcium carbonate, with some contribution of organic matter.

The equilibrium dependence between q and C_{eq} at a given C_S (Fig. 4) was described with Langmuir-type equation:

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

and the influence of C_S (Fig. 5) was described with the following dependence:

$$q_{eq}(C_S) = q_m \left(1-\frac{C_S}{d+C_S}\right) \quad (3)$$

where d is the sorbent concentration at which sorption capacity is $0.5q_m$.

The following model, describing sorption capacity as the function of equilibrium chromium(III) concentration and sorbent concentration was proposed:

$$q_{eq}(C_{eq}, C_S) = q_m \left(\frac{bC_{eq}}{1+bC_{eq}}\right)\left(1-\frac{C_S}{d+C_S}\right) \quad (4)$$

The model parameters for sorption carried out at different pH and temperature were determined by nonlinear regression (*Mathematica v. 3.0*) and are presented in Table 4. The sample experimental results for sorption at 20 °C, pH 5 were described with the model equation (Fig. 6). The model fitted the experimental data reasonably well, that was shown in Fig. 7 that compares model values with experimentally determined.

The proposed model consists of two equations: (1) the effect of equilibrium sorbate concentration (2), (2) the effect of sorbent concentration (3). The maximum sorption capacity that is possible to reach is q_m (maximum biosorption capacity). In Eq. (2), $q_{eq} = q_m$ at high C_{eq}, in Eq. (3), $q_{eq} = q_m$ at low C_S. This is achieved by the particular construction of the equations: the term $(bC_{eq}/(1+bC_{eq})) \to 1$ when $bC_{eq} \gg 1$, the term $1-(C_S/(d+C_S)) \to 1$ when $C_S \to 0$. Therefore, the maximum biosorption capacity of eggshells is reached

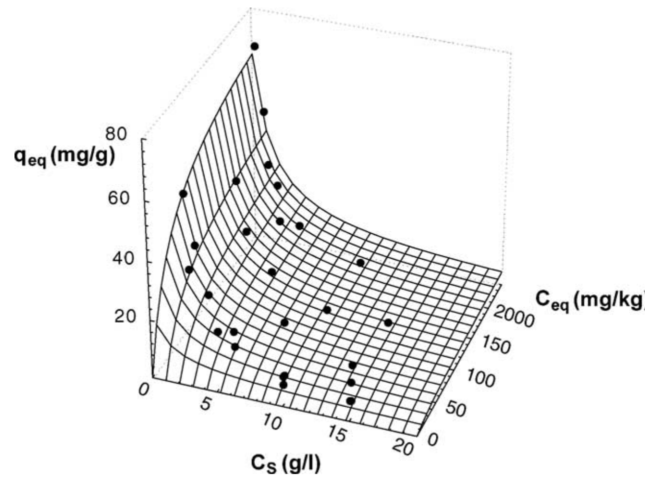

Fig. 6. Three-dimensional sorption surface showing model prediction (continuous surface) and experimental data points for biosorption at 20 °C, pH 5.

at high equilibrium sorbate concentration and low sorbent concentration.

Langmuir constant (b) describes how steep is the isotherm, this is so-called the affinity of sorbent to sorbate. The higher value of d is, the better affinity of sorbent to sorbate would be. d is the concentration of sorbent at which $q = 0.5q_m$. This means that d describes the effect of sorbent concentration on sorption capacity. It was showed that at low sorbent concentration higher sorption capacities are reached, at high sorbent concentration, low sorption capacity is obtained. Therefore, at $C_S \to 0$, $q \to q_m$. At $d \to 0$ at $C_S \to \infty$, $q \to 0$, but at $d \to \infty$, $q = q_m$ in the whole range of sorbent concentration. Therefore, low values of d mean that there is the strong influence of sorbent concentration on sorption capacity, high values of d show that the influence of sorbent concentration is the opposite.

By considering the model parameters of eggshells, the sorbent posseses the highest affinity to sorbate at the

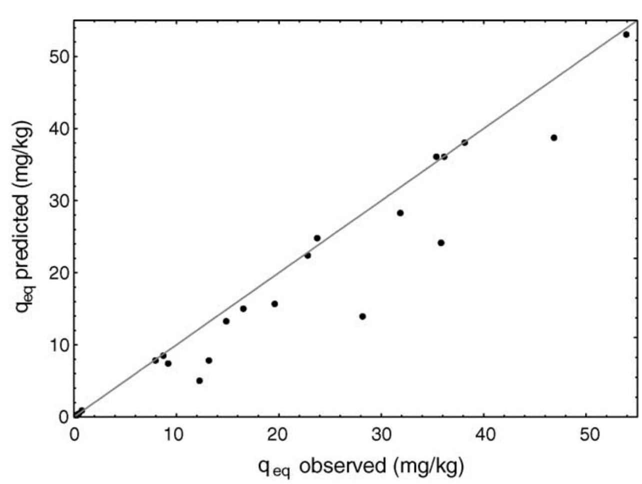

Fig. 7. Comparison of model predictions and experimental data for biosorption at 20 °C, pH 5.

temperature 20 and 60 °C at pH 5, and at 60 °C at pH 3. The effect of sorbent concentration on sorption capacity at pH 5 increases with temperature up to 50 °C and afterwards decreases, and at pH 3 is significantly higher at 60 °C when compared with 22 °C, pH 3 and 60 °C, pH 5. Therefore, if we would like to work on high concentrations of the sorbent (in order to reach the lowest possible concentration of metal ions), it would be advantageous to work at possible low values of parameter d, that is 20–40 °C, pH 5.

The effect of sorbent concentration on biosorption isotherm ($q_{eq} = f(C_{eq})$) was determined for sorbent concentration in the range 1–15 g/l. However the effect of sorbent concentration on biosorption capacity ($q_{eq} = f(C_S)$) at different initial Cr(III) ions concentration was studied for wider range of sorbent concentrations (0.1–25 g/l). The lowest concentration of the biosorbent, the highest biosorption capacity (according to the formula $q = (C_0 - C)/C_S$), however at lowest concentration the sorbent, there is also higher residual Cr(III) ions concentration. Therefore, if the objective is to achieve very low residual Cr(III) ions concentration, it is necessary to work on high concentration of the sorbent. At these conditions sorption capacity would be low. However, if the cost of the sorbent is not a problem (just like in the case of eggshells), it would be advantageous to perform the process at high sorbent concentrations in order to remove the highest possible quantities of Cr(III) ions.

The uptake of Cr(III) increased with increasing solution concentration and generally with decreasing sorbent concentration (Fig. 5). The maximum binding capacity of chromium was ca. 70 mg/g were observed at final Cr(III) solution in the region 200 mg/kg and at sorbent concentration <1 g/l (for sorption at 20 °C, pH 5).

It was observed that the maximum sorption capacity decreased with temperature (Fig. 2, Table 4). The parameter *d* representing the effect of sorbent concentration on sorption capacity, increased with temperature up to 50 °C and decreased at 60 °C. It was found that the parameter describing the effect of sorbent concentration on sorption capacity was influenced by temperature, since i.e. more intense dissolution of carbonates from eggshells might occur at higher temperatures. The confirmation of co-effect of sorbent concentration and temperature is the fact that equilibrium pH (at given initial pH) was the function of both temperature and sorbent concentration.

Table 4 shows maximum sorption capacity determined experimentally at C_S 1 g/l and as model parameter. It was found that the maximum biosorption capacity was reached at the lowest possible sorbent concentration. The experimental values are given for sorbent concentration 1 g/l, the model value q_m should be reached at $C_S \to 0$. Statistically significant correlation ($r = 0.90$, $p < 0.01$) was observed between these values. The parameter q_m was in general 2.6 times higher than q_{eq} values determined at C_S 1 g/l since q_m was the model parameter estimated at $C_S \to 0$ and $C_{eq} \to \infty$.

4. Conclusions

Among various metal sorbents (including biosorbents), a particular attention is paid to the identification of those that are cost-effective. If a sorbent is low-cost or is even a waste material, the process efficiency might be highly improved by increasing the concentration of a sorbent. In this work, eggshells were identified as a promising biological sorbent, since exhibited high sorption capacity. The present study showed that eggshells, a biological sorbent of animal origin, can find an application as biological sorbent of chromium(III) ions from aqueous solutions. The experiments were carried out only for Cr(III) as an example of metal cation, but it is supposed that eggshells would show similar sorption performance towards other cations, according to evaluated cation exchange capacity, that was evaluated as up to 4.4 meq/g. However, in order to confirm this, it is necessary to perform further investigations.

The effect of process parameters: concentration of pH, temperature, sorbent and sorbate on the process kinetics and pH and temperature on process equilibrium were studied. The uptake of chromium ions by eggshells, when the initial concentration of Cr(III) was 100 mg/kg and sorbent concentration was 1 g/l at 20 °C, pH 5 was evaluated as 15.2 mg/g. Under these conditions, 15% of Cr(III) ions were removed. Between 15 and 66% of Cr(III) ions were captured from the solution when the concentration of the sorbent was 1 and 15 g/l at initial concentration 100 mg/kg.

At low sorbent concentrations, high biosorption capacity is obtained, but low quantities of Cr(III) ions are removed from the solution. At high sorbent concentration, sorption capacity is low, but larger quantities of metal ions are bound. Low concentrations of metal ions can be used for the treatment of low concentration, large volume effluents. If treatment of concentrated effluents is planned, it is necessary to use higher concentrations of the sorbent. In this case sorbent will not be saturated with metal ions. The studied sorbent was able to remove Cr(III) to a level lower than permitted by environmental regulations, for instance at 40 °C, C_0 100 mg/kg, C_S 15 g/l. However, at 20 °C, C_0 200 mg/kg, pH 5, C_S 5 g/l, residual Cr(III) ions concentration would be 70 mg/kg. Eggshells were found to be an efficient sorbent with the maximum experimentally determined sorption capacity in the range 21–160 mg/g depending on pH and temperature. The maximum experimentally determined sorption capacity was obtained at 20 °C, pH 5.

The process kinetics was found to follow pseudo-second-order rate equation. The model fitted experimental data very well. The process equilibrium was reached after 60 min. It was found that the initial concentration of Cr(III) ions resulted in increase of equilibrium sorption capacity, similarly as temperature and pH. This effect on sorption rate constant was usually the opposite. It was found that the highest sorption capacities were reached at very low sorbent concentrations.

The equilibrium sorption capacity was described as the function of equilibrium concentration of chromium(III) ions and sorbent concentration. The influence of sorbent concentration was described with Langmuir-type equation and the influence of sorbate concentration, with the empirical dependence. The model fitted experimental data reasonably well. Model maximum sorption capacity was higher than determined experimentally, although a strong correlation between these values was observed.

Sorption performance of Cr(III) by eggshells was compared with other sorbents. It was found that its biosorption capacity was two times higher than activated carbon [22], comparable with animal bones [9], two times lower than blue-green algae *Spirulina* sp. [23]. Since the mechanism of biosorption by eggshells is probably ion-exchange to carbonate groups, it is expected that binding capability of other metals could be of similar magnitude. However, it is necessary to perform further investigations to confirm this hypothesis.

Acknowledgement

This research was financially support by Polish State Committee for Scientific Research (No. PBZ KBN 060/T09/2 001).

References

[1] J.T. Matheickal, Q. Yu, Biosorption of lead(II) from aqueous solutions by *Phellinus badius*, Miner. Eng. 10 (9) (1997) 947–957.
[2] S. Bailey, T.R. Olin, M.A. Dean, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (11) (1999) 2469–2479.
[3] K.S. Low, C.K. Lee, S.C. Liew, Sorption of cadmium and lead from aqueous solutions by spent grain, Process. Biochem. 36 (2000) 59–64.
[4] S. Babel, T.A. Kurniawan, Low-cost adsorbents for heavy metals uptake from contaminated water: a review, J. Hazard. Mater. B 97 (2003) 219–243.
[5] A.I. Zouboulis, M.X. Loukidou, K.A. Matis, Biosorption of toxic metals from aqueous solutions by bacteria strains isolated from metal-polluted soils, Process. Biochem. 39 (8) (2004) 909–916.
[6] J. Wang, Biosorption of copper(II) by chemically modified biomass of *Saccharomyces cerevisiae*, Process. Biochem. 37 (8) (2002) 847–850.
[7] K. Chojnacka, A. Chojnacki, H. Górecka, Trace element removal by *Spirulina* sp. from copper smelter and refinery effluents, Hydrometallurgy 73 (1/2) (2004) 147–153.
[8] F. Boukhlifi, A. Bencheikh, Characterization of natural biosorbents used for the depollution of waste water, Ann. Chim.-Sci. Mat. 25 (2000) 153–160.
[9] K. Chojnacka, Equilibrium and kinetic modelling of chromium(III) sorption by animal bones, Chemosphere 59 (3) (2005) 315–320.
[10] C.J. Williams, D. Aderhold, R.G.J. Edyvean, Comparison between biosorbents for the removal of metal ions from aqueous solutions, Water Res. 32 (1) (1998) 216–224.
[11] J.Z. Xie, C. Hsiao-Lung, J.J. Kilbane, Removal and recovery of metal ions from wastewater using biosorbents and chemically modified biosorbents, Bioresour. Technol. 57 (2) (1996) 127–136.
[12] Anonymous, Valuable raw materials extracted from egg shells, Food Eng. Int. 25 (2) (2000) 45–48.
[13] C. Davis, R. Reeves, High value opportunities from the chicken egg, A Report for the Rural Industries Research and Development Corporation, 2002.
[14] A. Schaafsma, I. Pakan, G.J.H. Hofstede, F.A.J. Muskiet, E. Van Der Veer, P.J.F. De Vries, Mineral, amino acid, and hormonal composition of chicken eggshell powder and the evaluation of its use in human nutrition, Poultry Sci. 79 (2000) 1833–1838.
[15] W. Daengprok, W. Garnjanagoonchorn, Y. Mine, Fermented pork sausage fortified with commercial or hen eggshell calcium lactate, Meat Sci. 62 (2) (2002) 199–204.
[16] G.D. Butcher, R. Miles, Concepts of Eggshell Quality 1, Fact Sheet VM-69, A Series of the Veterinary Medicine Department, Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida, 1996.
[17] R.D. Van der Weijden, J. Meima, R.N.J. Comans, Sorption and sorption reversibility of cadmium on calcite in the presence of phosphate and sulfate, Mar. Chem. 57 (1/2) (1997) 119–132.
[18] D. Wenming, G. Zhijun, D. Jinzhou, Z. Liying, T. Zuyi, Sorption characteristics of zinc(II) by calcareous soil-radiotracer study, Appl. Radiat. Isotopes 54 (3) (2001) 371–375.
[19] Y.S. Ho, G. McKay, Pseudo-second order model for sorption processes, Process. Biochem. 34 (1999) 451–465.
[20] A.B. Mukherjee, Chromium in the environment of Finland, Sci. Total Environ. 217 (1998) 9–19.
[21] Z. Aksu, Equilibrium and kinetic modelling of cadmium(II) sorption by *C. vulgaris* in a batch system: effect of temperature, Separ. Purif. Technol. 21 (2000) 285–294.
[22] S.I. Lyubchik, A.I. Lyubchik, O.L. Galushko, L.P. Tikhonova, J. Vital, I.M. Fonseca, S.B. Lyubchik, Kinetics and thermodynamics of the Cr(III) adsorption on the activated carbon from co-mingled wastes, Colloid. Surf. B 242 (2004) 151–158.
[23] K. Chojnacka, Biosorption of Cr^{3+}, Cd^{2+} and Cu^{2+} ions by blue-green algae *Spirulina* sp.: kinetics, equilibrium and the mechanism of the process, Chemosphere 59 (1) (2005) 75–84.