

Silica particles with N-methyl-D-glucamine for boron removal

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ABSTRACT

Silica particles were obtained by Stöber method in presence of N-methyl-D-glucamine. It was noted that amount of N-methyl-D-glucamine used to synthesis did not affect the physicochemical properties of prepared sorbents significantly. The investigated samples had similar content of nitrogen and were characterized by similar water uptake. The sorption behavior towards borates was investigated in a batch system at pH=9.5. The studies showed that sorption was controlled by the Langmuir mechanism and sample capacity was 0.2 mmol/g. The pseudo-second-order model described the boron sorption on prepared materials adequately.

Keywords: boron removal; silica; sorption; N-methyl-D-glucamine

INTRODUCTION

Boron is widely distributed in the environment, mainly in the form of borates that is difficult to remove from aqueous solutions. Boron is an element that can enter water supplies from natural sources or human-born activities [1]. It is used as flame retardants in plastics and cellulosic insulation, neutron absorbers, as a component of herbicides or fertilizers, and appears in washing powders or soaps [2, 3]. Due to its wide application boron concentration in groundwater range from 0.3 to more than 100 mg/L throughout the world [4]. Average surface water concentration of boron is about 0.1 mg/L but concentrations vary greatly, depending on boron content of local geologic formations and some anthropogenic sources.

Boron is a micronutrient essential for growing fruits and vegetables [5]. This is the element of special attention as its deficiency and excess are harmful for many plants [6, 7]. It plays an important role in the normal functioning of plants [6, 7] while its deficiency inhibits growth of meristematic tissue, disrupts normal cell formation and delays enzymatic reactions. In humans, small amounts of boron occur in all tissues. However, an excess of boron may lead to damage of cardiovascular, coronary, nervous and reproductive systems [7, 8]. Therefore, boron concentration in water and wastewater is regulated in many countries. The recommended boron content in drinking water, according to WHO guideline was set in 1998 to 0.5 mg/L and revised lately to 2.4 mg/L [9]. Some countries have their own regulations and most of them still keep 1 mg/L as the recommended value. That situation takes place in European Union while Canada recommends 5 mg/L and the United States 0.3 mg/L [10, 11].

In the recent years a significant increase in the concentration of boron in surface waters has been observed and water should be deboronated before its use. There is no universal method for removal of boron from aqueous solutions. Biological treatment, chemical precipitation and conventional ion exchange are ineffective methods. Sorption processes based on the use of chelating ligands as N-methyl-D-glucamine, membrane processes and hybrid processes [12, 13] are mostly employed for water deboronation.

In this study monodispersive silica particles modified with N-methyl-D-glucamine were evaluated as potential sorbents for boron removal from water. The particles were synthesized and characterized to determine their sorption properties.

EXPERIMENTAL

Materials

Tetraethyl orthosilicate 98% (TEOS) was purchased from Aldrich and used as delivered. N-methyl-D-glucamine >99% (NMDG) was delivered from Fluka. Ammonia water (25% aqueous solution of NH₃), ethanol 99.6 %, boric acid, NaOH were delivered by POCH.

Synthesis of SiO₂ particles

Silica particles were prepared by Stöber method by hydrolysis and condensation of TEOS in presence of NMDG. Two ratios of TEOS to NMDG (4:1 and 2:1) were used. When ammonia was added to the reaction mixture the samples named I and II were synthesized. When the reaction was carried out in presence of NMDG only the samples named III and IV were obtained. The silica particles were synthesized by mixing 8.0 g of TEOS with 50 mL of ethanol. After

homogenization the solution was continuously stirred with 1000 rpm and 2.0 or 4.0 g of NMDG was added. In the case of preparation of I and II samples, 2.5 mL of ammonia water was added very slowly. In the case on III and IV samples, 2.5 mL of water was added. The hydrolysis of SiO_2 was carried at room temperature within 24 h. To remove the unreacted components the suspensions were dialysed towards water with of cellulose dialysis tubing of 14 kDa cut-off. Composition of reactants is given in Table 1.

Analysis

The average diameter of synthesized particles was investigated using laser diffraction method by means of Mastersizer X (Melnerv Instruments GmbH, Germany).

Water regain ($W_{\text{H}_2\text{O}}$) was measured using centrifugation method by placing 0.5 g of swollen polymer in a fritted-glass column and centrifuging it for 5 min with 3000 rpm. The sample was weighted and dried at 105°C for 24 h. After cooling to room temperature the sample was weighted again. Water regain was calculated according to [14]

$$W_{\text{H}_2\text{O}} = \frac{m_w - m_d}{m_d} \quad (1)$$

where m_w is the weight of swollen polymer after centrifugation and m_d is the dry weight of polymer.

Nitrogen content was determinate by the Kjeldhal method after mineralization of the sample (about 200 mg) in concentrated sulfuric acid containing copper sulfate and potassium sulfate. The procedure is described elsewhere [14].

Batch-mode sorption

Sorption of boron was studied with 5 mg B/L solutions at $22 \pm 2^\circ\text{C}$. About 0.05 g of sorbent was gentle shaken with 50 mL of solution for 24 hours. After that time sorbent was filtered and concentration of boron was determinate by means of Azomethine-H method. The distribution coefficient ($\log K_B$) was calculated as a ratio of amount of boron adsorbed by 1 g of sorbent to the amount of boron in solution.

Sorption isotherms

The sorbent samples of 0.05 g were gently shaken with 100 mL of solutions containing 1 – 8 mg B/L ($\text{pH} = 9.5$) at $22 \pm 2^\circ\text{C}$ for 24 h. After that time boron concentration was determined. The maximum boron uptake (q_{max}) and the distribution of binding sites was calculated from Langmuir, Freundlich and Dubinin-Radushkevich isotherms.

Sorption kinetics

The used procedure was as follows: a flask with a capacity of 1000 mL was filled with sorbent to give a suspension of 0.1 g dry polymer/L. Boron solution (2 mg B/L, 500 mL) was added to the flask and mixed gently. Samples of solution of 3 mL were taken out at different time to determine boron concentration by means of Azomethine-H method.

Boron solutions

The boron solution was prepared with MiliQ water and reagent grade boric acid. The pH of the solution was adjusted with sodium hydroxide.

Analysis of boron

Through the studies, boron concentration was determined spectrophotometrically by means of Azomethine method ($\lambda_{\text{max}} = 410 \text{ nm}$). Jasco V-630 spectrophotometer was used for the measurements [4]. The boron standard solutions ranging from 0.5 to 2.5 mg B/L were applied for calibration.

RESULTS AND DISCUSSION

Preparation of SiO_2 particles

In the conducted syntheses NMDG was used to incorporate boron selective ligand to silica structure and to catalyze conversion of tetraethyl orthosilicate. The amine groups of N-methyl-D-glucamine react with TEOS according to scheme shown in Figure 1. It was observed that addition of NMDG reduced tendency of SiO_2 particles to aggregate. The distributions of particle size are given in Figures 2 and 3. It was noted that addition of ammonia to the reaction mixture did not affect size distribution but slightly enlarged the yield.

Table 1 Silica particles preparation

Sample	TEOS:NMDG ratio	TEOS/NMDG amount [g/g]	Ammonia water [mL]	Reaction yield [%]
I	4:1	8/2	2.5	85
II	2:1	8/4	2.5	55
III	4:1	8/2	-	82
IV	2:1	8/4	-	51

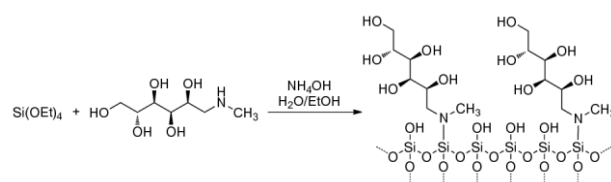


Figure 1 Synthesis of silica in presence of NMDG.

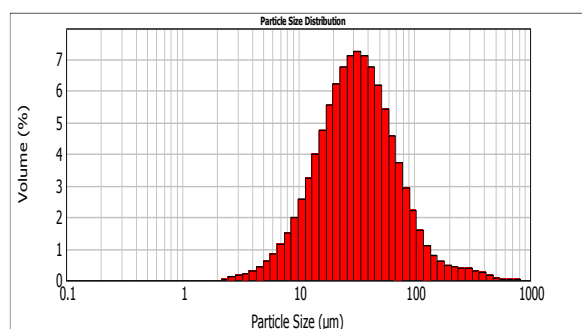


Figure 2 Diffraction pattern of silica particles. Sample I

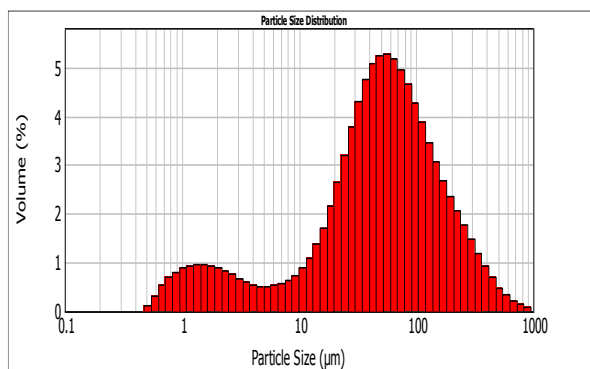


Figure 3 Diffraction pattern of silica particles. Sample II

The microscopic investigation of obtained particles revealed the presence of aggregates (Figures 4 and 5). In the pictures one can see large clusters of SiO_2 . It meant that NMDG located on the surface of silica particles did not fully protect them and large aggregates were formed. The microscopic investigations are in agreement with laser diffraction patterns: the particles with size of 60 micrometer can be seen.



Figure 4 Microscope picture of sample I (1000x)

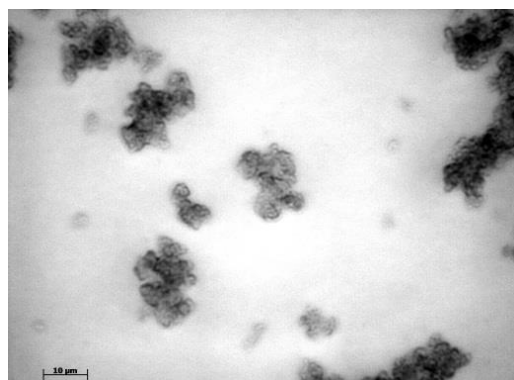


Figure 5 Microscope picture of sample II (1000 x)

After determination of basic morphological properties of the sorbents they were subjected to evaluation of the physico-chemical character. It was shown that content of nitrogen was about 0.8 mmol/g and water regain of 1.0 g/g was similar for all compared samples. That resulted in the comparable boron uptake for all investigated samples (Table 2).

Table 2 Physicochemical properties of materials

Sample	Z_N [mmol/g]	W_{H_2O} [g/g]	q_B [mg/g]	$\log K_B$
I	0.84	1.1 ± 0.05	1.7 ± 0.2	2.7
II	0.80	0.9 ± 0.04	1.5 ± 0.1	2.6
III	0.80	1.1 ± 0.07	1.7 ± 0.2	2.7
IV	0.78	0.9 ± 0.05	1.3 ± 0.15	2.4

Evaluation of sorption properties

The results of boron sorption are shown in Table 2. It can be stressed that amount of NMDG used in syntheses did not affect the value of boron uptake. Hence, to study sorption mechanisms we selected sample I and III. The experimental data are shown in Figure 6. For these data, the Langmuir, Freundlich and Dubinin-Radushkevich models were used to check which better described the phenomenon.

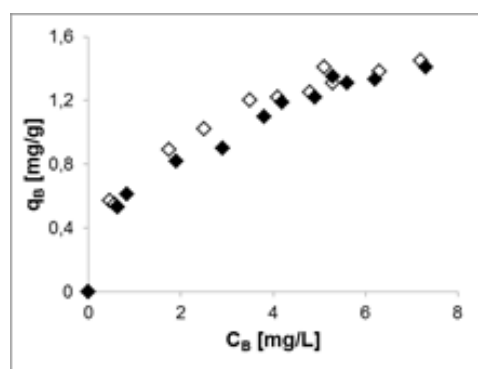


Figure 6 Sorption isotherms of sorbent I (open diamond) and sorbent III (filled diamond)

Langmuir isotherm. The equation was used to calculate the maximal uptake of boron (q_{max}) [15,16]:

$$q = \frac{q_{max} bc}{1 + bc} \quad (2)$$

where q was the uptake at equilibrium concentration (mmol/g), q_{max} was the maximal uptake (mmol/g), c was the bulk equilibrium concentration (mmol/L), b was a constant related to the free energy of adsorption (L/mmol).

Values of q_{max} and b were determined from the linear form of Langmuir isotherm (eq.3).

$$\frac{1}{q} = \frac{1}{q_{max} bc} + \frac{1}{q_{max}} \quad (3)$$

They are collected in Table 3.

The properties of both materials are the same with the maximum boron uptake of 0.2 mmol B/g (2.2 mg B/g).

Freundlich isotherm. This model is easily applicable when the experimental data are plotted in $\log q$ versus $\log c$ form (eq.4) [15,17].

$$\log q = m \log c + \log a \quad (4)$$

The model contains two fitting parameters a and m . For homogeneous materials m should be close to 1 while for heterogeneous m value approaches zero [15,17]. The calculated values for Langmuir and Freundlich models are collected in Table 3.

Table 3. Langmuir and Freundlich fitting parameters for samples A and C

Sample	Langmuir			Freundlich	
	$q_{\max}$ [mmol/g]	R^2	b [L/mmol]	m	R^2
I	0.16	0.988	9.05	0.835	0.972
III	0.19	0.986	9.30	0.824	0.959

The Freundlich model did not describe the sorption isotherm as well as Langmuir model did. Its R^2 parameters were smaller. Hence, we assumed that sorption followed the Langmuir's case.

Dubinin-Radushkevich isotherm. The sorption model helps to evaluate interaction between adsorbate and sorbent [17]. It is used to distinguish the kind of sorption nature: if it has physical or chemical origin.

$$\ln q = \ln q_{\max} - K_{DR} \varepsilon^2 \quad (5)$$

where $q_{\max}$ is the maximal adsorption capacity [mmol/g], K_{DR} is the Dubinin-Radushkevich constant [kJ²/mol²], ε is the Polanyi potential (equation 6):

$$\varepsilon = RT \ln\left(1 + \frac{1}{c}\right) \quad (6)$$

The fitting parameters for Dubinin-Radushkevich isotherm are listed in Table 4.

Table 4. The Dubinin-Radushkevich fitting parameters for samples I and III

Sample	$q_{\max}$ [mmol/g]	R^2	E [kJ/mol]
I	0.12	0.849	1.8
III	0.14	0.873	1.7

It looks that Dubinin-Radushkevich model did not describe adequately the experimental data – the calculated R^2 parameters were the worst among all evaluated models. Hence, the DR model was not applied for description of the sorption mechanism.

Kinetics of sorption

Kinetics of boron uptake is shown in Figure 7. For sample III, the maximal uptake was observed after 10 hours, while sample I needed 25 hours to reach that value. The differences disappeared at the very beginning of the process, when both samples showed very fast sorption kinetics (50% of maximal uptake was observed after 30 min). It was supposed that some differences appeared in mechanism of the sorption process. In order to evaluate that option, the diffusions and sorption kinetics models were compared.

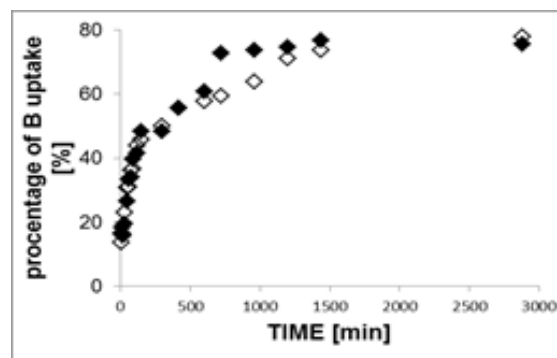


Figure 7 Kinetics of boron sorption on sorbent I (open diamond) and sorbent III (filled diamond).

Diffusion models

The kinetic data were fitted to diffusion models (equations 7 and 8) to check if the film diffusion or particle diffusion rates controlled the process [4,18,19].

$$k_a t = -\ln\left(1 - \frac{q_t}{q_e}\right) \quad (7),$$

where q_t and q_e represent the amount of adsorbed species (mmol/g) at any time t and at equilibrium time, respectively, and k_a represents the sorption rate constant for film diffusion process.

The second equation has a shape:

$$k_b t = -\ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right) \quad (8)$$

where k_b is the sorption rate constant for particle diffusion process.

The calculated values of k_a and k_b are collected in Table 5. For both evaluated sorbents, the sorption rate constants were similar for diffusion mechanisms and the correlation value did not allow distinguish which mechanism dominated. That means it was impossible to determine if film diffusion or particle diffusion was the limiting step.

Table 5 Diffusion models of sorption

Sample	$k_a t = -\ln\left(1 - \frac{q_t}{q_e}\right)$		$k_b t = -\ln\left(1 - \left(\frac{q_t}{q_e}\right)^2\right)$	
	k_a	R^2	k_b	R^2
I	0.006	0.971	0.004	0.977
III	0.006	0.953	0.003	0.957

Conventional sorption kinetics

In evaluation of sorption kinetics the pseudo-first and pseudo-second-order models are commonly used [18, 20]. The sorption kinetics for the pseudo-first model is given by eq. (9)

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad (9)$$

where q_t and q_e represent the amount of adsorbed species (mmol/g) at any time t and at equilibrium time, respectively, and k_1 represents the sorption rate constant (min⁻¹).

Integrating Eq. (9) with respect to boundary conditions $q=0$ at $t=0$, and $q=q_t$ at $t=t$, one obtains

$$\log(q_e - q_t) = \log(q_e) - \frac{k_1 t}{2.303} \quad (10)$$

Sorption rate constant k_1 can be calculated from the plot of $\log(q_e - q_t)$ vs. time.

The kinetic data can be analyzed by means of pseudo-second-order kinetics also:

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad (11)$$

where k_2 is the pseudo-second-order rate constant (g/mmol min).

Varying the variables in Eq. (11) one gets

$$\frac{dq_t}{(q_e - q_t)^2} = k_2 dt \quad (12)$$

and integrating Eq. (12) for the boundary conditions $q=0$ at $t=0$, and $q=q_t$ at $t=t$, one obtains the final form:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (13)$$

A plot t/q vs. t gives the value of constant k_2

The calculated values k_1 (1/min) and k_2 (g/mmol min) are listed in Table 6.

Table 6 Kinetic parameters of boron sorption

Sample	Pseudo-first		Pseudo-second	
	k_1	R^2	k_2	R^2
I	$1.84 \cdot 10^{-3}$	0.971	$2.51 \cdot 10^{-2}$	0.994
III	$2.99 \cdot 10^{-3}$	0.959	$2.74 \cdot 10^{-2}$	0.994

It can be seen that experimental data fit well to the pseudo-second-order mechanism of sorption and for that mechanism the sorption rate of sample III is a little larger than sample I. That finding is in agreement with observation of boron sorption shown in Figure 7 when sample III adsorbed boron faster than sample I.

CONCLUSIONS

We have demonstrated the method for synthesis of silica particles with N-methyl-D-glucamine ligands. We have determined the following properties of obtained sorbents:

- i) the size distribution of synthesized materials was independent on the amount of used components,
- ii) the method of preparation and amount of added N-methyl-D-glucamine did not affect the physicochemical properties of obtained samples,
- iii) sorption properties of synthesized sorbents were similar for material prepared with or without of ammonia,

iv) boron sorption followed the Langmuir isotherm while kinetics was well-described by the pseudo-second model.

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