

# Cross-Linked Chitosan Spheres and Magnetic Composites for Adsorption of Heavy Metals and Catalysis

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The paper presents the results of a study of the adsorption properties chitosan (CS) spheres cross-linked with epichlorohydrin (ECH). During the study, a procedure was developed for obtaining and cross-linking of CS spheres, as well as CS-based magnetically separable composites. The adsorption capacity of CS-ECH spheres was tested by the example of aqueous solutions of  $\text{Ni}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  with different concentrations. It was shown that in a batch mode the adsorption equilibrium in the case of  $\text{Ni}^{2+}$  was achieved in 60 min, whereas in the case of  $\text{Cr}_2\text{O}_7^{2-}$  a longer time was required (420 min or more). It was found that CS-ECH spheres can accumulate about 3 wt.%  $\text{Ni}^{2+}$  and up to 10 wt.% of  $\text{Cr}^{6+}$  ions. Magnetically separable composites ( $\text{Fe}_3\text{O}_4$ -CS-ECH) were found to provide higher efficiency of adsorption in comparison with CH-ECH. Moreover, the catalyst Pd/CH-ECH was synthesized and tested in hydrogenation of nitrobenzene at ambient pressure.

## 1. Introduction

Heavy metals (Ni, Pb, Cd, Hg, Cu, Zn, Cr, etc.) are one of the most common pollutants of industrial wastewater, which have toxic effects on living organisms (Ahmad et al., 2021). The human body requires a minimum concentration of heavy metals to cause poisoning and stimulate the development of various diseases. Thus, proper treatment of industrial wastewater before its discharge into the ecosystem is of paramount importance (Saha et al., 2019).

Adsorption is one of the most convenient methods of wastewater treatment. The efforts of researchers are constantly focused on the development of new adsorbents that would be inexpensive, effective, environmentally safe and reusable. Chitosan (CS) and its chemically modified derivatives have attracted much attention as promising sorbents (Ahmad et al., 2017). It is noteworthy that CS is a natural polysaccharide obtained by deacetylation of chitin – the second most common biopolymer available in nature, after cellulose.

Along with biodegradability and cheapness, CS demonstrates excellent adsorption properties due to the presence of functional groups (amino and hydroxy groups) in its main chain, which act as active centers for the adsorption of metal ions. However, the direct use of CS as an adsorbent is difficult due to its high crystallinity, low mechanical strength and instability in an acidic medium (the solubility of CS in a medium with  $\text{pH} < 4$  is its main disadvantage). The chemical and mechanical stability of CS-based materials can be improved by modifying it (Vidal and Moraes, 2019), in particular, by covalent cross-linking. The use of cross-linking agents, such as epichlorohydrin (ECH), glutaraldehyde (GA), as well as the use of other methods of chemical modification, can significantly improve the physical, chemical and biological properties of CS. Moreover, for the removal of heavy metal ions the use of composite CS-based materials is promising.

This work is devoted to the synthesis of the sorbent in the form of cross-linked CS spheres. ECH was used as a cross-linking agent as shown in Figure 1.

It should be noted that ECH is a common cross-linking agent used in polysaccharide chemistry (Crini and Morcellet, 2002). This functional agent contains two reactive groups (the epoxy group and the chloroalkyl part), which can form bonds with the -OH and -NH<sub>2</sub> groups of CS. Magnetically separable composites based on cross-linked CS spheres containing  $\text{Fe}_3\text{O}_4$  particles were also synthesized. The adsorption of  $\text{Ni}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions from aqueous solutions was studied using the obtained cross-linked CS spheres. Besides, catalytic study of NB hydrogenation was carried out using Pd/CS-ECH system.

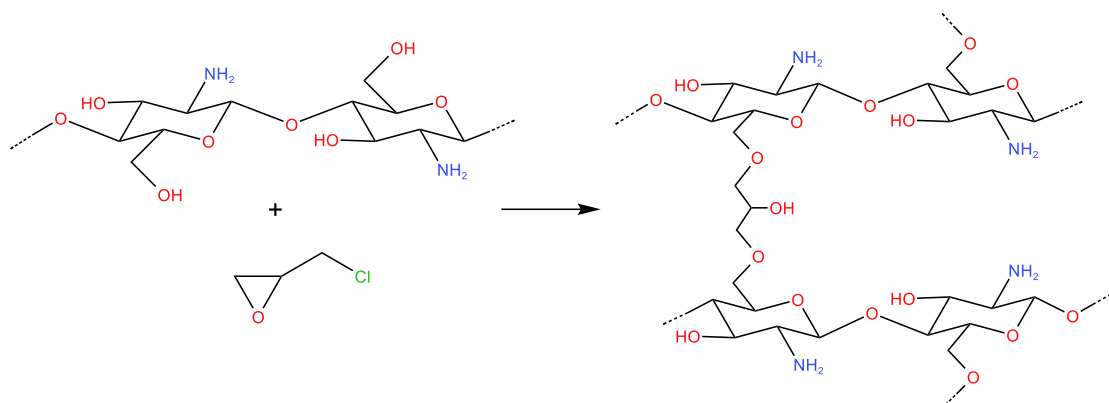


Figure 1: Scheme of CS cross-linking with ECH

## 2. Experimental

### 2.1 Preparation of CS-ECH spheres

CS produced by Fluka, BioChemika with a molecular weight of ~ 400 kDa and an average viscosity (200-400 MPa\*s for 1 % solution in 1 % acetic acid at 20 °C) was used for the preparation of spheres. CS (2 wt.%) dissolved in 1 % acetic acid. CS spheres (diameter ~ 2 mm) were obtained by dripping of CS solution in acetic acid into an aqueous NaOH solution (1 mol/L) at constant stirring (100 rpm) at a temperature of 25 °C.

Freshly prepared CS spheres were introduced into a glass reactor containing 20 mL of NaOH solution (1 mol/L) at constant stirring (100 rpm). After reaching the operating temperature (40 °C), 1 mL of ECH was introduced into the reactor. Cross-linking duration was 24 h. The resulting CS-ECH spheres were thoroughly washed with distilled water and dried at 65 °C for 24 h. After drying, nearly double decrease of the diameter of CS-ECH spheres was found.

To obtain a magnetically separable composite ( $\text{Fe}_3\text{O}_4$ -CS-ECH), 0.001 g of preliminarily synthesized magnetic particles ( $\text{Fe}_3\text{O}_4$ ) was mixed with 8 mL of CS solution and then dripped into NaOH solution (1 mol/L). The cross-linking of the obtained magnetically separable spheres was carried out according to the procedure described above for non-magnetic adsorbents.

The resulting CS-ECH and  $\text{Fe}_3\text{O}_4$ -CS-ECH spheres are presented in Figure 2.

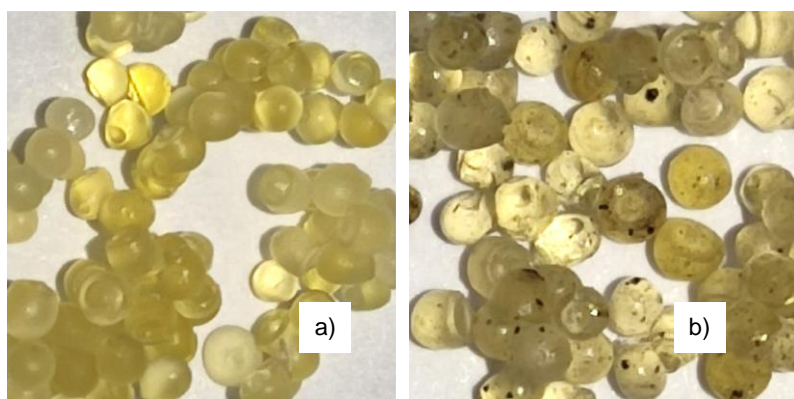


Figure 2: Pictures of dried CS-ECH (a) and  $\text{Fe}_3\text{O}_4$ -CS-ECH (b) spheres

### 2.2 Adsorption studies

The adsorption of  $\text{Ni}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions from aqueous solutions (the pH of distilled water was 5.8) was studied at 25 °C using the obtained cross-linked CS-based spheres, for the preparation of which  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  and  $\text{K}_2\text{Cr}_2\text{O}_7$  salts were used. It should be noted that the pH of aqueous solutions of nickel chloride was lower by 1-1.5 units compared to the pH of distilled water used for their preparation.

The duration of absorption was 60 min in the case of nickel chloride solutions and 420 min in the case of potassium bichromate solutions. To study the adsorption process in a batch mode, a series of samples

containing precise amounts of cross-linked CS-based spheres and aliquots of the studied solutions were prepared. The mass ratio of a solution to sorbent was 200 / 1. After a certain time, the cross-linked CS-based spheres were separated, and the optical density of the solution was measured using a UV5Bio spectrophotometer (Mettler Toledo, USA) in the wavelength range of 200-1100 nm. The concentrations of  $\text{Ni}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions were determined on the basis of corresponding calibration dependencies.

It is noteworthy that in aqueous solutions with a pH of about 6.0, most of the  $\text{Cr}^{6+}$  exists in the form of  $\text{HCrO}_4^-$  (75 wt.%) and  $\text{CrO}_4^{2-}$  (25 wt.%) (Vieira et al., 2014). During the spectrophotometric analysis of  $\text{K}_2\text{Cr}_2\text{O}_7$  solutions, a certain volume of HCl solution (1 mol/L) was added to the aliquot of the sample to identify the absorption region of  $\text{Cr}_2\text{O}_7^{2-}$  ions with a maximum at a wavelength of 440 nm.

Adsorption of  $\text{Ni}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  was also studied in continuous mode at 25 °C using peristaltic pump. In each experiment a cartridge was filled with 300 mg of CS-ECH spheres. The solution of  $\text{Ni}^{2+}$  or  $\text{Cr}_2\text{O}_7^{2-}$  (200 mL with concentration of 10 mmol/L) was constantly circulating through the sorbent layer (flow rate 100 mL/min).

### 2.3 Synthesis and testing of Pd-CS-ECH catalyst

The catalyst Pd-CS-ECH (Pd content of 1 wt.%) was synthesized by the adsorption method. The calculated amount of  $\text{Na}_2\text{PdCl}_4$  (59.9 wt.% of Pd) was dissolved in aqueous solution of NaCl with the addition of HCl. Then, CS-ECH spheres were placed into Pd-containing solution until this solution became colorless (30 min). Resulting Pd-CS-ECH was thoroughly washed with distilled water and used for hydrogenation of nitrobenzene (NB) to aniline (AN). Hydrogenation was carried out at 70 °C, ambient pressure and constant stirring (1000 rpm) using *i*-PrOH- $\text{H}_2\text{O}$  mixture (1 : 1) as a solvent. NB loading was 1 mmol; 50 mg of the catalyst was used;  $\text{NaBH}_4$  (3 mmol) was chosen as a hydrogen source. Samples of reaction mixture were periodically taken and analyzed via GC-MS (Shimadzu GCMS-QP2010S) equipped with a capillary column HP-1 (100 m x 0.25 mm i.d., 0.50  $\mu\text{m}$  film thickness). The concentrations of the reaction mixture components were calculated using the internal standard calibration method (diphenylamine was used as an internal standard).

## 3. Results and discussion

### 3.1 Effect of ions' concentration in a batch mode

The effect of concentration of  $\text{Ni}^{2+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions as well as the duration of adsorption was studied in a batch mode. As shown in Figure 3, the adsorption of  $\text{Ni}^{2+}$  proceeds within 60 min, however the adsorption capacity is nearly independent on the initial concentration of  $\text{Ni}^{2+}$  and remains about 30-32 mg/g.

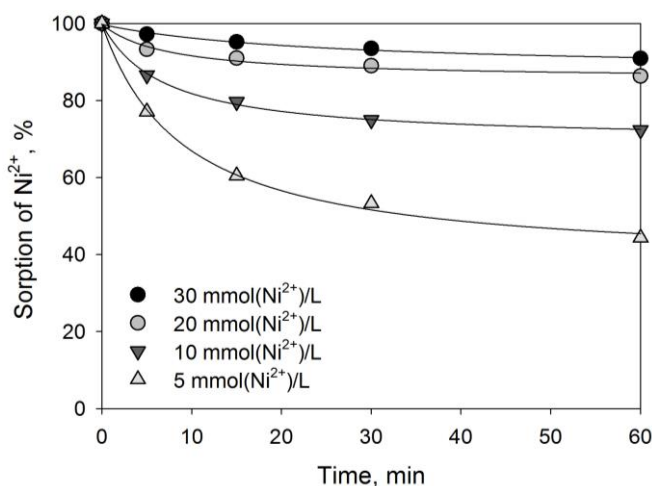


Figure 3: Effect of the initial concentration of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  on kinetic curves of  $\text{Ni}^{2+}$  uptake

In the case of  $\text{Cr}_2\text{O}_7^{2-}$ , the adsorption proceeds slow. The adsorption capacity calculated with respect to  $\text{Cr}^{6+}$  increases from 24.8 mg/g up to 101.4 mg/g with corresponding increase of the initial concentration of  $\text{K}_2\text{Cr}_2\text{O}_7$  from 5 mmol/L up to 30 mmol/L, as shown in Figure 4.

Also, based on the data presented in Figures 3 and 4, it is obvious that in the case of nickel chloride solutions, the adsorption equilibrium is achieved in a relatively short time (about 60 min), whereas in the case of potassium bichromate solutions with the same concentration, much longer time is required (more than 420 min). This observation can be explained by the fact that  $\text{Ni}^{2+}$  cations can be coordinated with functional

groups (-OH and -NH<sub>2</sub>) of CS. Thus, as soon as all the adsorption sites become occupied with nickel, the adsorption process nearly stops. In contrast, Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> ions interact with the surface of CS-ECH spheres and penetrate into their volume undergoing, along with chemical adsorption, multilayer physical adsorption, as was shown in the work of Kekes et al. (2021). It was found that for CS-ECH spheres the adsorption of Cr<sup>6+</sup> ions was well fitted with the Temkin isotherm, which takes into account both chemical and physical adsorption. The standard deviation between the experimental data and the isotherm model was 0.9999.

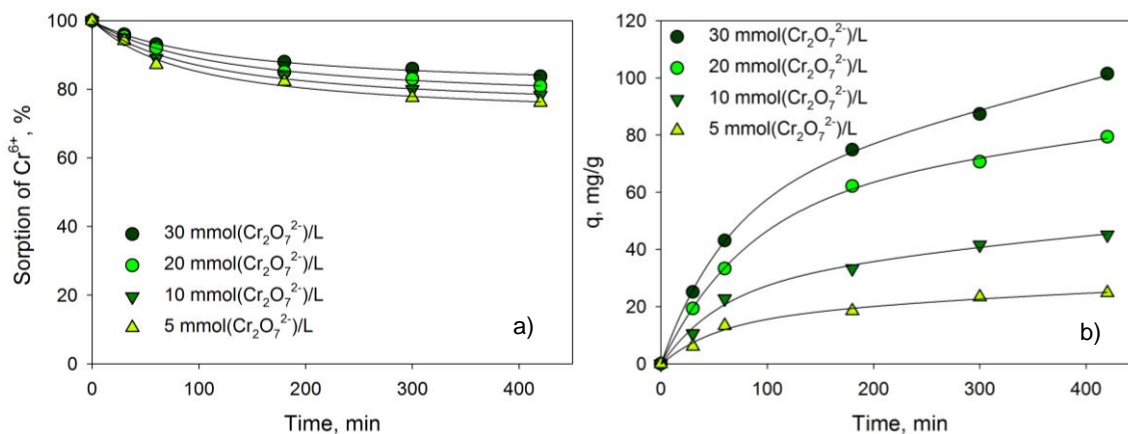


Figure 4: (a) Effect of the initial concentration of K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> on the kinetic curves of Cr<sup>6+</sup> uptake, (b) and the adsorption capacity of CS-ECH

Synthesized magnetically separable composites (Fe<sub>3</sub>O<sub>4</sub>-CS-ECH) were found to be promising sorbents, which possessed higher adsorption capacity in comparison with CS-ECH, as shown in Figure 5, and allowed simple and effective magnetic separation from solutions by applying external magnetic field.

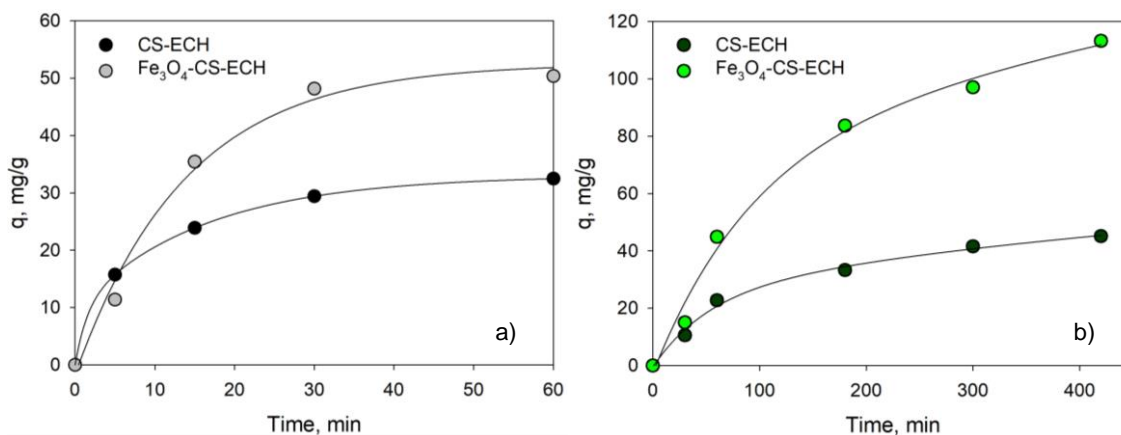


Figure 5: Comparison of adsorption capacities of CS-ECH and Fe<sub>3</sub>O<sub>4</sub>-CS-ECH with respect to Ni<sup>2+</sup> (a) and Cr<sup>6+</sup> (b) at the initial concentrations of Ni<sup>2+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> equal to 10 mmol/L

It was found that CS-ECH spheres are effective sorbents and can accumulate about 3 wt.% Ni<sup>2+</sup> (this value is virtually independent on the initial concentration of nickel ions in the selected range) and from 2.5 wt.% up to 10 wt.% of Cr<sup>6+</sup> ions. Table 1 shows a comparison of the adsorption capacity of some materials known from literature with the obtained CS-ECH and Fe<sub>3</sub>O<sub>4</sub>-CS-ECH spheres.

As can be seen from the presented data, obtained CS-based adsorbents, especially the magnetically separable ones, possess good adsorption ability. However, CS-ECH and Fe<sub>3</sub>O<sub>4</sub>-CS-ECH are second to such materials, as CS-DEO-SP that is CS cross-linked with diepoxyoctane (DEO) and modified with spermine (SP) allowing enrichment of the adsorbent with nitrogen and hence providing the remarkably high adsorption capacity with respect to heavy metals.

Table 1: Comparison of adsorbents

Adsorbent	Ion	Concentration	Adsorption capacity (q), mg/g	Ref.
CS-ECH	Ni <sup>2+</sup>	from 5 mmol(Ni <sup>2+</sup> )/L	32.0	This work
Fe <sub>3</sub> O <sub>4</sub> -CS-ECH		up to 30 mmol(Ni <sup>2+</sup> )/L	50.3	
CS-ECH	Cr <sup>6+</sup>	10 mmol(Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> )/L	45.1	This work
Fe <sub>3</sub> O <sub>4</sub> -CS-ECH			113.2	
CS-ECH		30 mmol(Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup> )/L	101.4	
Dolomite	Ni <sup>2+</sup>	20 mg/L	20.1	(Khoshraftar et al, 2023)
CS-bentonite clay cross-linked with GA	Cr <sup>6+</sup>	from 10 ppm up to 260 ppm	106.4	(Altun, 2020)
CS-DEO-SP	Cr <sup>6+</sup>	500 mg/L	352.0	(Vakili, 2019)

### 3.2 Adsorption in continuous mode

Results of the adsorption studies in continuous mode are presented in Figure 6. As it can be seen, in the case of Ni<sup>2+</sup> the adsorption capacity was nearly the same as for batch experiments (29.2 mg/g), while in the case of bichromate ions 122.9 mg/g was reached that is 2.7 times higher in comparison with the adsorption capacity found in a batch mode (see Figure 5b).

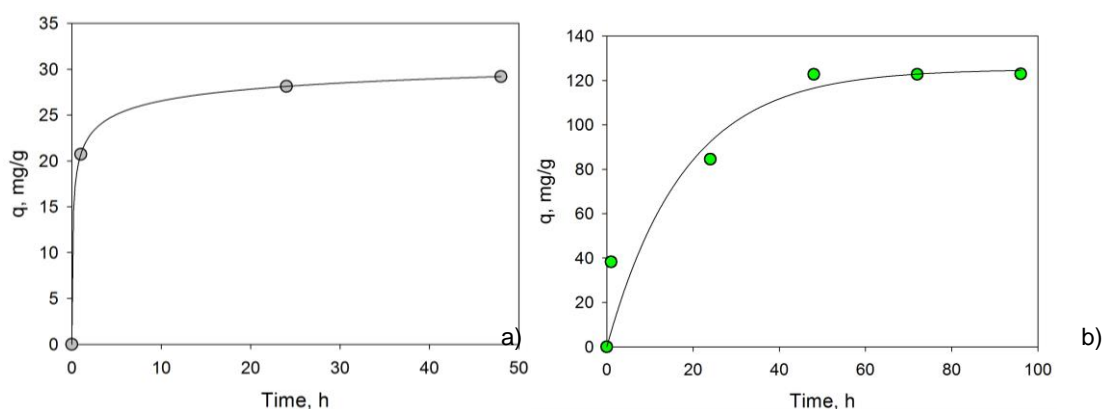


Figure 6: Adsorption capacities of CS-ECH with respect to Ni<sup>2+</sup> (a) and Cr<sup>6+</sup> (b) at the initial concentrations of Ni<sup>2+</sup> and Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> equal to 10 mmol/L

### 3.3 Catalytic study

The results of catalytic testing of the synthesized 1%-Pd/CS-ECH in the reaction of NB hydrogenation to AN using sodium borohydride as a hydrogen source are shown in Figure 7.

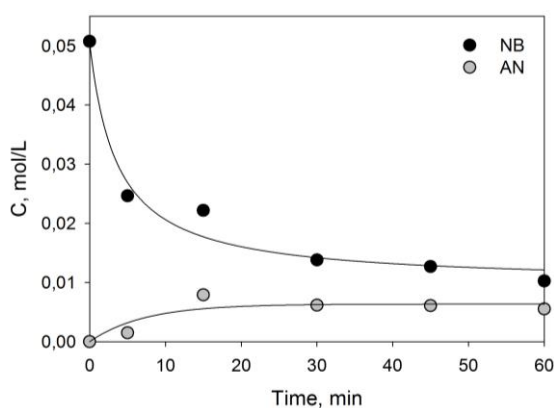


Figure 7: Kinetic curves of NB conversion and AN accumulation (1000 rpm, 70 °C, ambient pressure, solvent i-PrOH-H<sub>2</sub>O (1 : 1), 1 mmol of NB, 3 mmol of NaBH<sub>4</sub>, 50 mg of 1%-Pd/CS-ECH)

As it can be seen, NB conversion proceeded rather fast and reached 80 % by 60 min of the reaction. However, the selectivity with respect to AN was low (about 17 %). Among the side products, azoxybenzene prevailed, while nitrozobenzene was the main intermediate product. Thus, further optimization of CS-based catalytic systems along with the reaction conditions should be provided.

#### 4. Conclusions

In the framework of this work, CS spheres cross-linked with ECH (CS-ECH) and their magnetically separable analogue ( $\text{Fe}_3\text{O}_4$ -CS-ECH) were synthesized using CS with a molecular weight of 400 kDa. The obtained spheres were shown to be promising adsorbents for water purification from heavy metals by the example of  $\text{Ni}^{2+}$  and  $\text{Cr}^{6+}$ , allowing to achieve an adsorption capacity of about 30 mg/g in the case of  $\text{Ni}^{2+}$  and 100-123 mg/g in the case of  $\text{Cr}^{6+}$ . It is noteworthy that, in contrast to nickel, the adsorption capacity with respect to chromium ions depended on the initial concentration, which was likely due to the different mechanisms of their adsorption. Moreover, it was found that CS-ECH adsorbents can be successfully applied in a continuous mode since the layer of spheres (each of 1 mm in diameter) has very low resistance to the flow. The adsorption capacity of magnetically separable  $\text{Fe}_3\text{O}_4$ -CS-ECH composites exceeded the adsorption capacity of CS-ECH by 1.5-2.5 times, depending on type of adsorbed ion.

Besides, the catalyst 1%-Pd/CS-ECH was synthesized by the adsorption of  $\text{PdCl}_4^{2-}$  ions from slight acidic aqueous solution. Freshly prepared catalyst was tested in hydrogenation of NB to AN at 70 °C and ambient pressure using sodium borohydride as a hydrogen source. It was found that 80 % of NB conversion can be achieved for 60 min of the reaction. However, the selectivity with respect to AN was only about 17 % that requires further optimization of catalyst synthesis procedure and reaction conditions.

#### Acknowledgments

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