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CHITOSAN-BASED HYROGEL FOR INDUSTRIAL WASTE TREATMENT

HYDROŻEL NA BAZIE CHITOZANU DO OCZYSZCZANIA ŚCIEKÓW PRZEMYSŁOWYCH

Abstract

The method of chitosan-based hydrogel synthesis from chitosan, aspartic acid and ethylene glycol under microwave irradiation is presented in this article. Application of microwave radiation enables to reduce the reaction time and elimination of catalyst from reaction mixture. Synthesised hydrogel is examined as sorption agent for metal ions ($\text{Fe}^{2+/3+}$, Zn^{2+} and Hg^{2+}) within 12 h and 168 h and sorption capacity is calculated.

Keywords: aspartic acid, chitosan, hydrogels, industrial waste, microwave radiation

Streszczenie

W artykule przedstawiono metodę otrzymywania hydrożelu na bazie chitozanu, kwasu asparaginowego i glikolu etylenowego w polu promieniowania mikrofalowego, co pozwala na skrócenie czasu reakcji oraz wyeliminowanie katalizatora ze środowiska reakcji. Otrzymany hydrożel zbadano pod kątem wykorzystania jako czynnika sorpcyjnego dla jonów metali ($\text{Fe}^{2+/3+}$, Zn^{2+} i Hg^{2+}) w ciągu 12 h i 168 h, a także obliczono pojemność sorpcyjną.

Słowa kluczowe: kwas asparaginowy, chitozan, hydrożel, ścieki przemysłowe, mikrofa

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Abbreviations

AA	– aspartic acid
EG	– ethylene glycol
FTIR	– Fourier Transform Infrared Spectroscopy
GPC	– Gel Permeation Chromatography
RI	– Refractive Index (detector)
PEG/PEO	– poly(ethylene glycol)/poly(ethylene oxide)
M_w	– weight average molecular weight [g/mol]

1. Introduction

Industrial waste recycling is nowadays an important issue in environmental protection. Recovery of different metals from manufacturing waste allows for the reduction of production costs and prevents infiltration of toxic compounds to the natural environment. Particularly dangerous are trace amounts of metals like mercury, cadmium, lead, zinc and chromium. Therefore, the elimination and recycling of such refuse products are of crucial significance to industrial waste treatment. Sorption techniques are the most popular methods for this assignment. Application of a suitable sorption agent, especially of natural origin, enables complete elimination of metal from waste and its recycling [1-4]. The basic parameter characterising such an agent is sorption capacity, which is related to the amount of adsorbed metal on a unitary mass of sorption agent and is described as:

$$m_a = A \cdot m = V \cdot (c_0 - c_a) \quad (1)$$

where:

A – sorption capacity – mass of adsorbed metal [mg] on a unitary mass of sorption agent [g],

V – volume of solution during sorption [l],

c_0 and c_a – initial and final concentration of adsorbed metal in solution, respectively [mg/l],

m_a – mass of adsorbed metal [mg].

What is more, the selective sorption of heavy metals from alkali metals solution is a very intractable problem in wastewater treatment. Chitosan, which is a derivative of chitin, has been recently used for such an application [5–9]. However, chitosan is soluble in water below pH = 6.3, which generates difficulties in controlling and regeneration of adsorbing bed. In the Department of Chemistry and Technology of Polymers at Cracow University of Technology a new method of microwave-assisted synthesis of copolymer of chitosan and aspartic acid cured with ethylene glycol is developed. The application of microwave radiation allows to control reaction conditions and eliminates the exigencies of catalyst utilization. In aqueous solution chitosan-based polymer forms insoluble hydrogel selectively adsorbing heavy metal ions, especially from very diluted solutions.

2. Synthesis and characterisation of chitosan-based hydrogel

Chitosan-based hydrogel is synthesised in a polycondensation reaction, where a copolymer of chitosan and aspartic acid is formed and cured with ethylene glycol. The complete synthesis procedure was described in previous articles [10, 11].

The reaction is carried out in a multimode Milestone START Labstation microwave reactor within the power range of 230–270 W, with temperature rising from 80 to 110 °C in 44 min. Polycondensation by-product in the form of water is removed from the reaction mixture with the use of the Dean-Stark trap. The obtained dark red copolymer is washed with methanol, water, and dried at 80°C.

FTIR analysis of chitosan-based hydrogel demonstrates a wide band in a range of 3500–3100 cm^{-1} from stretch vibrations of OH and NH_2 groups. At 2940, 1450 and 1310 cm^{-1} symmetric and asymmetric stretch vibrations of CH_2 groups in the chitosan pyranose ring are observed. An additional band at 2890 cm^{-1} as well as a doublet at 1080 and 1040 cm^{-1} are related to methylene and hydroxyl groups from incorporated ethylene glycol, respectively. At 1640 cm^{-1} stretching vibrations in C=O and bending vibrations in N-H forming amide group, additionally blurred because of ester bonds formed between AA and EG placed in the same wave region, can be observed. Moreover, amide bonds are formed in the reaction of chitosan amino groups and aspartic acid carboxyl groups. Free carboxyl groups from AA or formed during microwave degradation of chitosan are visible at 1720 cm^{-1} [6, 12]. A medium band at 1390 cm^{-1} from C-H bending vibrations in N-acetyl group of chitosan and in a range of 1155–1040 cm^{-1} from the glycoside bond can be observed. A proposed structure of chitosan/AA copolymer cured with EG is presented in Fig. 1.

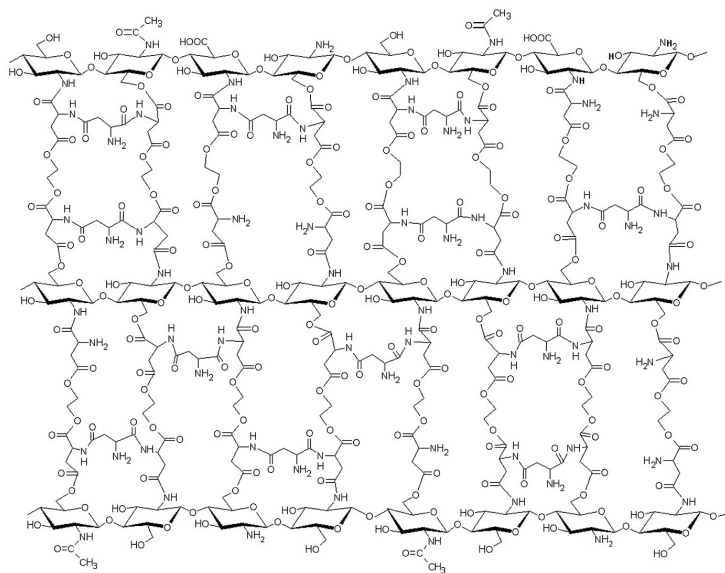


Fig. 1. Proposed structure of chitosan-based hydrogel

Rys. 1. Proponowana struktura hydrożelu na bazie chitozanu

Copolymer degradation in aqueous medium at room temperature in 30 days can be investigated with the use of GPC method. A sample (20 μl) is analysed on Knauer Smartline chromatograph with RI detector and POLYSEP-GFC-P4000 (Phenomenex) column. The

mobile phase is water with flow rate 0.5 ml/min and temperature 35 °C. The weight average molecular weight is calculated with the use of PEG/PEO standards.

After the reaction hydrogel is not purified to estimate all water soluble solution components. Only 8% of the polymer by weight with M_w of 500 000 g/mol dissolves in water and those parameters remain unchanged during 14 days. Afterwards the degradation process slightly accelerates. The molecular weight of initial chitosan is 400 000 g/mol. Moreover, a peak from unreacted GE used as a curing agent and diluter, can be observed, whereas no unreacted AA is detected. Surface carboxyl groups formed during the thermal degradation dissociate in aqueous medium giving $\text{pH} \approx 4$.

3. Determination of sorption capacity

Model wastes for hydrogel's sorption capacity determination are solutions of salts with the initial concentration of 100 ppm containing $\text{Fe}^{2+/3+}$, Zn^{2+} and Hg^{2+} ions, respectively. The investigation is divided into two steps: the first step is the determination of sorption capacity of unmodified chitosan and chitosan-based hydrogel during 12 h, and the second step is the determination of the same process but during 168 h (7 days). The sorption agent in amount of 1 g is placed in a closed plastic container and filled with 100 cm^3 of salt solution. The volume of 0.2 cm^3 solution is sampled every 1 h or 24 h, depending on the investigation step. The process is carried out at room temperature in two independent series called P1 and P2. The concentration of metal in the solution is determined with colorimetric methods [13, 14].

4. Results and discussion

The changes of metal concentration in solution during 12 h of sorption on chitosan bed are presented in Fig. 2.

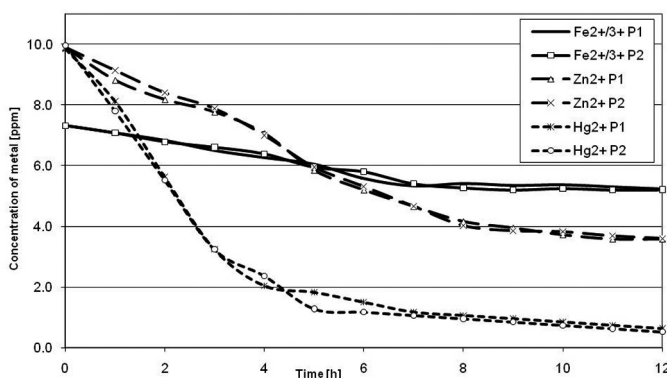


Fig. 2. Change of metal concentration during 12 h of sorption on chitosan bed

Rys. 2. Zmiany stężenia jonów metali w czasie 12 h sorpcji na złożu chitozanowym

The highest decrease in metal concentration during the 12 h sorption is observed for Hg^{2+} ions. A lower initial concentration of $\text{Fe}^{2+/3+}$ ions is a consequence of the oxidation reaction with the use of atmospheric oxygen forming $\text{Fe}(\text{OH})_3$ insoluble in water. The changes in metal concentration in the solution during 12 h of sorption on chitosan-based hydrogel bed are presented in Fig. 3.

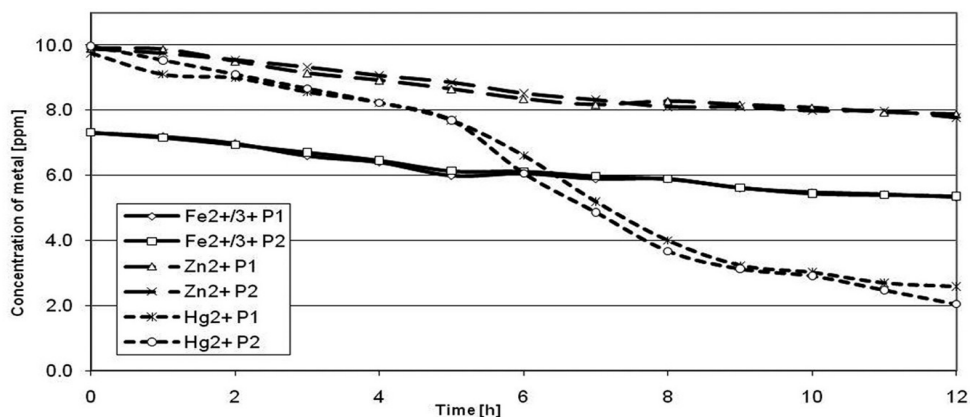


Fig. 3. Change of metal concentration during 12 h of sorption on chitosan-based hydrogel bed

Rys. 3. Zmiany stężenia jonów metali w czasie 12 h sorpcji na złożu hydrożelu na bazie chitozanu

The reaction of chitosan's amino and hydroxyl groups partaking in metal ions bonding causes a decrease in the sorption capacity of hydrogel [15, 16]. The minor decrease of metal concentration during 12 h of sorption is observed for Zn^{2+} and $\text{Fe}^{2+/3+}$ ions, whereas the major decrease of metal concentration is observed for Hg^{2+} ions.

Sorption capacity after exposure of the sorption agent for 12 h in the metal ions solution is calculated on the basis of the results presented in Fig. 1 and 2, equation (1) and mass of the sorption agent used. The results of the calculations are presented in Table 1.

Table 1

Sorption capacity of chitosan and chitosan-based hydrogel after 12 h

Sample		Sorption capacity [mg/g]		
		$\text{Fe}^{2+/3+}$	Zn^{2+}	Hg^{2+}
Chitosan	P1	2.09	6.32	9.23
	P2	2.11	6.30	9.45
	average	2.10	6.31	9.34
Hydrogel	P1	1.96	2.03	7.18
	P2	2.01	2.14	7.94
	average	1.98	2.08	7.56

The highest sorption capacity after 12 h of exposition is received for unmodified chitosan. Chemical modification of chitosan influences its chemical and physical properties and can be used for the synthesis of a material with defined sorption capacity.

The second research step includes sorption of the same metal ions on unmodified chitosan and hydrogel bed under the same conditions, but during 168 h (7 days). Ion concentration in the solution is determined every 24 h. The changes of metal concentration in the solution during 168h of sorption on unmodified chitosan are presented in Fig. 4.

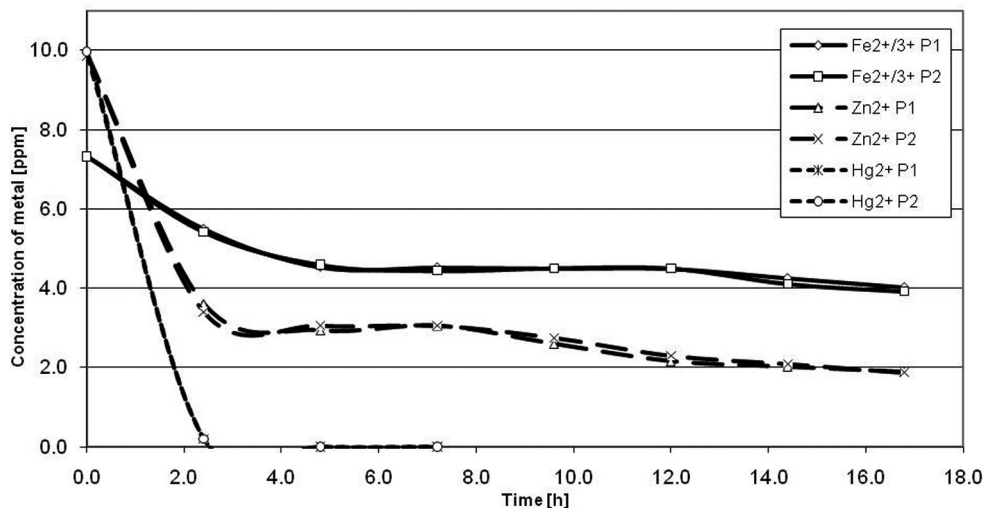


Fig. 4. Change of metal concentration during 168 h of sorption on chitosan bed

Rys. 4. Zmiany stężenia jonów metali w czasie 168 h sorpcji na złożu chitozanowym

After 24 h of sorption on unmodified chitosan no Hg²⁺ ions are detected. Colorimetric analysis of mercury concentration is carried out with the use of dithizone method with sensitivity of 0.1 ppm. The ions of iron and zinc after 7 days of sorption are still detected in the solution, however the concentration is reduced to about 53% and 20% of the initial amount for Fe^{2+/3+} and Zn²⁺, respectively. The changes of metal concentration in the solution during 168 h of sorption on chitosan-based hydrogel are presented in Fig. 5.

After 72 h of sorption on chitosan-based hydrogel no Hg²⁺ ions are detected. The ions of iron and zinc after 7 days of sorption are still detected in the solution and the concentration is reduced to about 70% and 65% of the initial amount for Fe^{2+/3+} and Zn²⁺, respectively. Sorption capacity after exposure of the sorption agent for 168 h in the metal ions solution is calculated on the basis of the results presented in Fig. 3 and 4, equation (1) and mass of the sorption agent used. An exception is the sorption capacity for mercury ions calculated after 3 days. The results of the calculations are presented in Table 2.

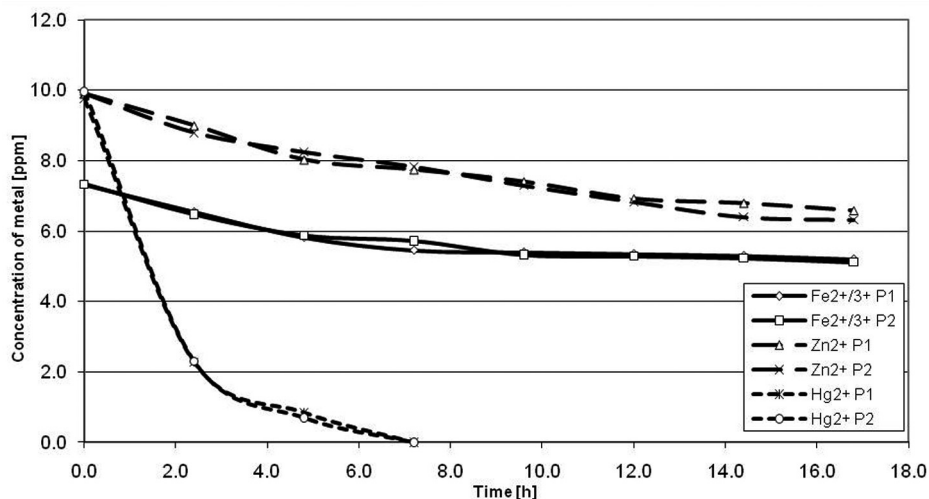


Fig. 5. Change of metal concentration during 168 h of sorption on chitosan-based hydrogel bed

Rys. 5. Zmiany stężenia jonów metali w czasie 168 h sorpcji na złożu hydrożelu na bazie chitozanu

Table 2

Sorption capacity of chitosan and chitosan-based hydrogel after 168 h

Sample		Sorption capacity [mg/g]		
		Fe ^{2+/3+}	Zn ²⁺	Hg ²⁺
Chitosan	P1	3.30	8.01	9.90
	P2	3.40	8.03	10.0
	average	3.35	8.02	9.95
Hydrogel	P1	2.12	3.32	9.78
	P2	2.22	3.59	10.0
	average	2.17	3.45	9.89

5. Conclusions

The reaction of chitosan and aspartic acid in ethylene glycol leads to the copolymer formation with properties of hydrogel. The process is carried out under microwave irradiation, which significantly reduces the reaction time and eliminates the catalyst from the reaction mixture. High temperature and microwave irradiation accelerate degradation of chitosan, however molecular weight of the obtained product is higher than that of the substrate. The obtained copolymer is analyzed with the use of FTIR method which confirms chemical bonding between chitosan, aspartic acid and ethylene glycol. Hydrogel is chemically stable in aqueous medium for 14 days and afterwards the degradation process slightly accelerates.

The obtained results of sorption capacity determination confirm a potential application of chitosan and chitosan-based hydrogel in industrial waste treatment. Sorption capacity is dependent on time and atomic mass of a metal ion. Hg^{2+} ions are completely removed from the solution after 24h on chitosan bed and 72 h on hydrogel bed, gaining $A = 10 \text{ mg/g}$. For light metal ions ($\text{Fe}^{2+/3+}$, Zn^{2+}) an equilibrium state is gained, which significantly reduces the sorption capacity.

Unmodified chitosan exhibits higher sorption capacity due to the higher content of free amino and hydroxyl groups partaking in metal-polymer complex formation. However, chitosan is soluble in a slightly acidic medium forming a highly viscous solution. The modification of solution pH is required to eliminate this problem. Simultaneous addition of base to the waste leads to dissolving the previously precipitated contamination. The obtained hydrogel is chemically stable, insoluble and insensible to solution pH.

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