

POROZNI ADSORPCIONI MATERIJAL U FORMI MIKROSFERA NA BAZI LIGNINA, FUNKCIONALIZOVAN NANOČESTICAMA MAGNETITA, ZA EFIKASNO UKLANJANJE HROMATNIH ANJONA

LIGNIN BASED POROUS, MICROSPHERE-SHAPED ADSORBENT FUNCTIONALIZED WITH MAGNETITE NANOPARTICLES FOR EFFECTIVE CHROMATE ANIONS REMOVAL

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Cilj istraživanja ovog rada predstavlja novu sintezu amino-modifikovanog adsorpcionog materijala na bazi prirodnog polimera, kraft lignina, dopunski funkcionalizovanog nanočesticama magnetita, za efikasno uklanjanje hromatnih anjona iz vodenog rastvora. Lignin mikrosfere obogaćene amino-grupama (LMS-NM) su dobijene postupkom inverzne kopolimerizacije iz suspenzije lignina u vodi, uz dodatak razgranatog poli(etilen-imina), i uz upotrebu sredstva za umrežavanje epichlorhidrina. Porozna struktura sintetisanih mikrosfera je formirana korišćenjem 5,0 mas. % natrijum-alginata. Dodatna efikasnost u uklanjanju anjona hroma postignuta je funkcionalizacijom sa nanočesticama magnetita (NM) dobijenog koprecipitacijom i dopunskim uvođenjem amino-grupa. Strukturne karakteristike sintetisanih LMS-NM adsorbenata su potvrđene primenom Furijeove infracrvene spektroskopije (FTIR). Morfologija i prečnik sintetisanih LMS-NM mikrosfera (500 - 800 μm) analiziran je primenom optičke mikroskopije. Uklanjanje hromatnih anjona iz vodenog rastvora izvršeno je u šaržnom sistemu pri čemu je potvrđena efikasnost i potencijal sintetisanih LMS-NM mikrosfera kao prirodnog adsorpcionog materijala poreklom iz nusproizvoda drvne industrije, za uklanjanje jona teških metala. Ovo istraživanje finansiralo je Ministarstvo prosvete, nauke i tehnološkog razvoja Republike Srbije u okviru projekata 451-03-9/2021-14/200325 i 451-03-9/2021-14/200135, uz doprinos projekta COST akcije br. CA17128.

Ključne reči: lignin; funkcionalizacija; nanomagnetit; porozne sfere; adsorbent

Research goal of this paper represents a novel method of synthesis of an amino-modified, highly effective natural polymer adsorbent kraft lignin based, functionalized with magnetite nanoparticles, for effective removal of chromate anions from water solution. Amino-modified lignin microspheres (LMS-NM) were synthesized via inverse suspension copolymerization of kraft lignin with poly(ethylene imine) grafting-agent and epichlorohydrin cross-linker. The porous structure of the synthesized adsorbent was formed using a 5.0 wt.% sodium-alginate solution. Additional efficiency in the removal of chromium anions from water was achieved by functionalization of lignin microspheres with magnetite (NM) nanoparticles obtained by co-precipitation and additional introduction of amino groups. Structure of formed LMS-NM was confirmed via Fourier Transform Infrared (FTIR) Spectroscopy. Optical microscopy analyses showed the creation of sphere-shaped materials and showed the diameter of prepared LMS-NM in the range of 500 to 800 μm. The removal of chromate anions from water

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solution was performed in a batch system. The result confirmed high adsorption efficiency and potential application of this nature-based adsorbent for heavy metal anions removal. This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, as part of the following projects: 451-03-9/2021-14/200325 and 451-03-9/2021-14/200135, with the contribution of the COST Action CA17128.

Key words: lignin; functionalization; magnetite nanoparticles; porous spheres; adsorbent

1 Introduction

Heavy-metal ions present in water are well-recognized for its toxicity, adverse and potentially carcinogenic effects to human health, and thus represent a worldwide concern. Hexavalent chromium, Cr(VI), one of the most toxic contaminants present in water, is released in the environment due to various anthropogenic activities, and significant efforts are made for its removal from water.

An increased interest of researchers is oriented in the synthesis and modification of biopolymers, nature-based adsorbents for removal of chromates and other heavy metal ions in wastewater [1]. Main biopolymers combined in biomass are lignin, cellulose and hemicelluloses. Lignin is one of the most abundant, low-cost, renewable sources of aromatic structures, which offers a wide range of high-value applications, and already in its pure form has a solid capacity to adsorb heavy-metal ions [2]. Its high adsorption capacity is a result of lignin's complex three-dimensional, highly cross-linked macromolecule composed structure, including coniferyl, sinapyl, and p-coumaryl alcohols, although high complexity might represent a challenge. As a revalorized secondary source, lignin can be extracted from the waste by-product from the pulp and paper industry or biomass pretreatment processes, mainly in a form of a kraft lignin and lignosulfonate. Kraft lignin is a kind of industrial lignin obtained from kraft pulp, which accounts for about 85% of the total lignin production in the world, according to Chen et al. (2015) in lignocellulose biorefinery feedstock engineering. Traditionally, kraft lignin is burnt for utilizing its energy potential, although due to its properties, abundance, low cost, and eco-friendliness, offers a potential high efficient bio-adsorbent for water treatment and removal of various heavy-metal ions [3–5].

Magnetic nanoparticles, such as iron oxide (Fe_3O_4) nanoparticles, are a potential wastewater treatment agent and can be used for the removal of contaminants from water [6]. Increased interest in its use is due because of their large surface area, high stability and, in particular due to potential reusability and extraction from water solutions, owing to its magnetic properties in a magnetic field [7].

Research efforts are also targeted to explore various sizes, active surface areas and adequate geometries of the adsorbents, coupled with the knowledge that the adsorption capacity very much depends on the functionalization and textural properties of the adsorbent, *i.e.* on the specific surface and porosity. Microsphere-shaped adsorbents provide a larger surface area and possess better diffusion, dispersion, and mass transfer behavior and various chemical modification and functionalization are efficient methods for improving its adsorption properties [8]. In our research, we successfully produced functionalized kraft lignin-based microspheres, providing a larger surface area and possessing better diffusion, adsorption and mass transfer behavior, in comparison to traditional adsorbents, for the removal of heavy-metal ions from water. In addition, our research focus is directed towards the synthesis of porous magnetite particles of nanometer size with the aim to coat the synthesized adsorbent and to provide the increase of the specific surface area and adsorption capacity for heavy-metal anions from water. Nanoparticles with excellent magnetic properties enable easy separation of used adsorbent and its recovery from water.

In this paper, we are presenting a novel synthesis method for preparation of amino-modified lignin microspheres, coated with nano-magnetite particles, showing excellent adsorption removal efficiency of toxic chromate anions from water solution.

2 Experimental section

The inverse suspension copolymerization of kraft lignin with poly(ethylene imine) grafting-agent and epichlorohydrin cross-linker, coupled with additional functionalization with nanoparticles of iron oxide (magnetite), was used for production of the LMS-NM adsorbent. The final goal is to further increase the adsorption capacity of heavy-metal anions removal from water solutions.

2.1 Materials

The materials used in the experiments were as follows: kraft lignin produced by Sigma-Aldrich, Germany; epichlorohydrin, $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ purchased by Merck Schuchardt, Germany; liquid paraffin oil and poly(ethylene imine) PEI, produced by Sigma-Aldrich, Germany, sodium alginate, synthesized locally, sodium dodecylbenzene sulfonate and $\text{NH}_3 \cdot \text{H}_2\text{O}$ produced by Centrohem, Serbia. Standard solution (AAS) of Cr(VI) was used for adsorption experiments with chromium anions. Deionized water was used in the experiments.

2.2 Synthesis of magnetic nanoparticles (NM)

Magnetic iron oxide nanoparticles were synthesized via the co-precipitation method and additionally amino-functionalized [9]. Briefly, 1.5 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 4.1 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 100 mL of deionized water under N_2 atmosphere. Further, 25 mL of 25% $\text{NH}_3 \cdot \text{H}_2\text{O}$ was briefly added to the mixture while applying magnetic stirring. As soon as $\text{NH}_3 \cdot \text{H}_2\text{O}$ was added, precipitation of magnetite took place. Following it, the dispersion was heated to 80 °C; when the set temperature was reached, 1 mL of oleic acid was added drop-by-drop through the funnel within 1 h. Finally, using the 30 mL of toluene the synthesized magnetic nanoparticles were extracted from the solution and kept at 4 °C for further use.

2.3 Synthesis of LMS-NM

The inverse suspension copolymerization method developed by Ge et al. [10] and further optimized in our previous research [11] was used as a base for LMS-NM synthesis, with additional development and upgrade by several modifications. Typically, 0.5 g of kraft lignin and 10 mL deionized water were added into a three-neck flask while stirring, followed by 2.0 g of PEI, 0.1 g of sodium dodecylbenzene sulfonate, and 10 mL of a 5.0 wt.% sodium alginate solution. Following the procedure provided in the 2.3 section of this paper, in-situ synthesized magnetite nanoparticles were added to the mixture. After mixing for several minutes this aqueous phase was added to oil phase of 80 mL of liquid paraffin and formed a suspension. After 30 min stirring the temperature was elevated to 60 °C. 2.0 mL of epoxy chloropropane was added drop-by-drop while stirring for 120 min to allow cross-linking copolymerization to take place. Following the centrifugation, the solid phase was rinsed with petroleum ether, ethanol and water. After 24 h lyophilization at -40 °C, the LMS-NM adsorbent was further characterized.

2.4 Characterization methods

Fourier transforms infrared (FTIR) spectra of LMS-NM were recorded in absorbance mode using the Nicolet™ iS™ 10 FT-IR Spectrometer (Thermo Fisher Scientific) spectrometer equipped with Smart iTR™ Attenuated Total Reflectance (ATR) Sampling accessories, in a range of 400-4000 cm^{-1} , 20 scan mode and 4 cm^{-1} resolution. The shape and size of LMS-NM adsorbent particles were analyzed through optical microscopy analysis using SMTV Visor Inspection System (Michael Bruch, Germany) at 15x e-zoom. Textural characteristics of synthesized lignin microspheres were determined using the Brunauer, Emmett, Teller (BET) method of analyzing nitrogen adsorption isotherms through the Micromeritics ASAP 2020 instrument. The influence of mass of the LMS-NM adsorbent and contact time on adsorption efficiency of chromate anions were studied in a batch test, measured on inductively coupled plasma mass spectrometry (ICP-MS) system, Agilent 7500ce from Waldbronn, Germany, equipped with an octopole collision/reaction cell. Relative standard deviation of all chromate anions investigated was between 1.3–5.1%.

2.5 Point of zero charge

The point of zero charge of the synthesized LMS-NM adsorbent was determined by the pH drift method. This analysis is undertaken to explore the influence of pH on the state of equilibrium of ionic/anionic species and protonation/deprotonation of LMS-NM functional groups [6].

2.6 Batch Adsorption Experiments

The adsorption efficiency and the effects of the diffusion process were studied in the batch adsorption experiments. Thermo SCIENTIFIC Laboratory shaker (Digital Heating/Shaking Drybath) was used to support the determination of the LMS-NM adsorption performances. Mass of the LMS-NM adsorbent was varied (1.0, 5.0, 7.5 and 10 mg) in the 10 ml of the standard solutions of chromate anions at initial concentration, C_i 10 mg L⁻¹ and pH 6.5. The experiments were performed at the following temperatures 25 °C, 35 °C and 45 °C, using the mean value of three determinations to evaluate the experimental data. The adsorption capacity of LMS-NM for the adsorbed chromate anions was calculated by using Eq. (1):

$$q = \left(\frac{C_i - C_f}{m} \right) \times V \quad (1)$$

where q represents adsorption capacity (mg g⁻¹), C_i , C_f are the initial and final concentration of chromate anions (mg L⁻¹), respectively, m mass of adsorbent (g) and V is a solution volume (L).

3 Results

3.1 FTIR Spectroscopy

Lignin, lignin microspheres (LMS) and fully functionalized LMS in a form of LMS-NM were characterized by FTIR spectroscopy. The broad band at 3380 cm⁻¹ in the FTIR spectra of our samples is assigned to aliphatic and aromatic O-H stretching vibration. The bands around 1601 cm⁻¹ contribute to the aromatic skeletal vibrations [10], indicating the aromatic structures of lignin, LMS and LMS-NM. The key difference of the FTIR spectrums of LMS-NM in comparison to lignin and LMS are the bands within the region of 1460 cm⁻¹ – 1025 cm⁻¹ ascribed to the stretching vibration of the C-N bond, and the band which originates from the tensile vibrations O – H is shifted to a wavelength of 3259 cm⁻¹ [10]. Between ~ 530 - 670 cm⁻¹ the curves differ slightly and indicate the presence of nanomagnetite in the structure.

3.2 Optical Microscopy

The optical microscopy was used to confirm the sphere shape and determine the average diameter of the synthesized LMS-NM adsorbent, as shown on the Figure 1. Relatively uniformed, slightly uneven spherical shapes are formed after the synthesis due to the influence of the functionalization with nanoparticles of magnetite. The average diameter of the LMS-NM adsorbent is in the range of 500 to 800 μm.

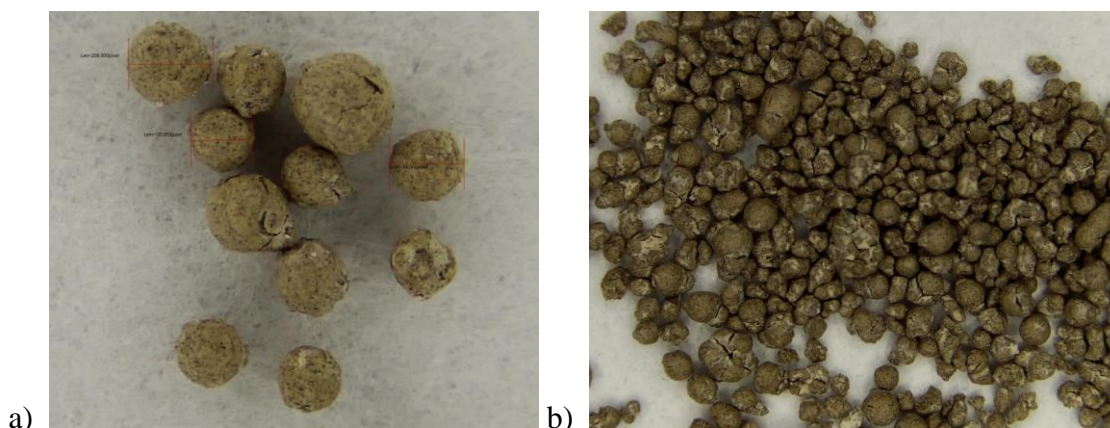


Figure 1. Sphere-shaped lignin microspheres functionalized with nanomagnetite

3.3 Textural characteristics

A porous surface area of the adsorbent with magnetite nanoparticles introduced, and the presence of a micro/mesopores in the structure are very important contributor for an effective adsorption process. The porous structure of the synthesized LMS-NM microspheres was formed using a sodium-alginate solution, while the role of the functionalization with nanoparticles of magnetite is to additionally support the efficiency of this porous adsorbent material. Specific active surface, volume and pore diameter of synthesized LMS-NM adsorbent, determined by analyzing nitrogen adsorption isotherms according to the BET method, are presented in Table 1. The adsorbent is mesoporous; the S_{BET} value of LMS-NM is 2.1 times higher than S_{BET} of kraft lignin ($1.8 \text{ m}^2/\text{g}$) contributing to the improvement of the adsorption of heavy metal anions from water [10].

Table 1. Textural characteristics of LMS-NM adsorbent

Sample	$S_{BET}, \text{m}^2/\text{g}$	$V_{total}, \text{cm}^3/\text{g}$	$V_{meso}, \text{cm}^3/\text{g}$	D_{mn}, nm	D_{max}, nm
LMS-NM	3.81	0.0228	0.0224	10.95	20.25

S_{BET} - specific surface; V_{total} - total pore volume; V_{meso} - volume of mesopores; D_{mn} - mean pore diameter and D_{max} - pore diameter of pores occupying most of the volume

3.4 pH_{pzc} determination

The point of zero charge (pH_{pzc}) represents the pH value where the surface charge density is equal to zero, and the surface potential is a directly result of the presence of a surface charge. The solid surface of the adsorbent is positively charged when pH value is less than pH_{pzc} and consequently negatively charged if pH values are above the pH_{pzc} value.

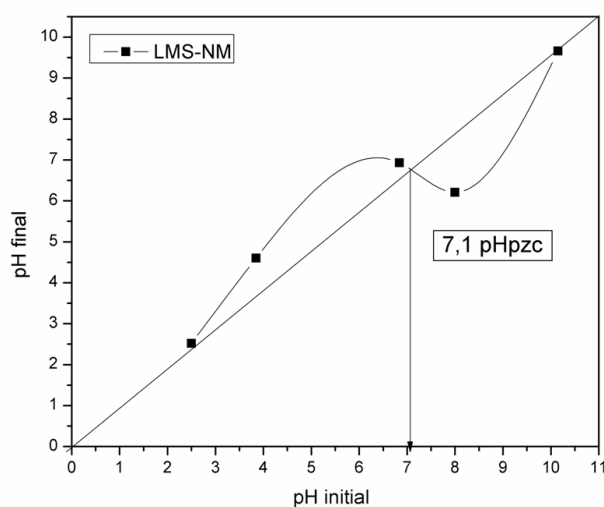


Figure 2. Determination of pH_{pzc} of LMS-NM adsorbent

Functional groups influence the charge of the adsorbent, and in case of the LMS-NM adsorbent, hydroxyl, methoxy and thiol groups [8] are covering its active surface. Therefore, it is important to support the interactions of the surface functional groups and chromate anions from water solution. The calculated LMS-NM adsorbent's pH_{pzc}, based on the experimental results, is presented in the Figure 2. The selection of pH 6.0 for chromate anions removal was in line with the results and the theoretical base for reaching the highest adsorption potential of LMS-NM.

3.5 Adsorption results

The adsorption experiments using LMS-NM adsorbent were performed at 25 °C, 35 °C and 45 °C to study the influence of the temperature on the adsorption efficiency. The Langmuir 1 isotherm model was utilized (Eq. 2). For the estimation of the thermodynamic parameters of adsorption, the Gibbs free energy equation and the van't Hoff linear equation (Eqs. 3, 4), i.e. van't Hoff plot, were calculated [6]:

$$q_e = (Kq_{\max}C_e)/(1 + KC_e) \quad (2)$$

$$\Delta G^\circ = -RT \ln K_L \quad (3)$$

$$\ln K_L = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (4)$$

where C_e is the equilibrium concentration of ions (mol l^{-1}), q_e represents the molar amount of adsorbed ions per weight of LMS-NM at equilibrium in mol g^{-1} , K and K_L represent Langmuir constants related to sorption affinity (l mg^{-1} and l mol^{-1} , respectively), and q_{\max} is maximum sorption capacity (mol g^{-1}). In Eqs. 2,3 ΔG° represents the change of free energy (kJ mol^{-1}), ΔH° the change of enthalpy (kJ mol^{-1}), ΔS° the change of entropy (kJ mol^{-1}), T the absolute temperature (K), and R being the ideal gas constant ($0.008314 \text{ kJ mol}^{-1}\text{K}^{-1}$).

The results of the Langmuir 1 adsorption isotherm and thermodynamic parameters at various temperatures for chromate anions are presented in Table 2. Langmuir 1 adsorption isotherm plots of LMS-NM are presented in Figure 3.

Table 2. Langmuir isotherm and thermodynamic parameters of LMS-NM adsorbent for chromate anions obtained at 25 °C, 35 °C and 45 °C, pH 6.0

Sample	$T, ^\circ\text{C}$	$q_e, \text{mg g}^{-1}$	$K, \text{L mg}^{-1}$	R^2
LMS-NM	25	62.92	0.15	0.99
	35	66.91	0.15	0.99
	45	70.75	0.16	0.99
	$T, ^\circ\text{C}$	$\Delta G^\circ, \text{kJ mol}^{-1}$	$\Delta S^\circ, \text{J mol}\cdot\text{K}^{-1}$	
	25	-35.06	137.04	
	35	-36.41		
	45	-37.80		

The results presented in Table 2 show an increase of adsorption capacity as the temperature increases, while Langmuir constant remains constant and very slightly increases at the highest temperature. According to the Langmuir isotherm, assumed mechanism of chromate anions adsorption is attributed to the monolayer adsorption with equal enthalpy and energy for all reactive sites [6]. Obtained negative ΔG° values from -35.06 to $-37.80 \text{ kJ mol}^{-1}$ indicate that adsorption occurs via spontaneous reactions followed by both physisorption and chemisorption mechanisms [6]. Slight decrease of ΔG° with temperature increase can be seen, indicating more feasible desolvation and diffusion at higher temperatures [6]. Positive value of ΔS° indicate the increase in disorder on the boundary solid-liquid layer [6].

4 Conclusions

Amino-modified lignin microspheres with functionalized magnetite nanoparticles in its structure (LMS-NM), obtained through an optimized novel method of inverse suspension copolymerization synthesis and in-situ functionalization, represent a highly effective natural polymer adsorbent, kraft lignin based, for effective removal of chromate anions from water solution. Based on a kraft lignin, originating from industrial waste streams, cross-linked with epichlorohydrin using poly(ethylene imine) grafting-agent and a 5.0 wt.% sodium-alginate solution - the highly-porous, microsphere-shaped adsorbent was formed. Further, in-situ functionalization with magnetite (NM) nanoparticles obtained by co-precipitation and amino coated additionally supported the chromate anion adsorption. Porous structure and active surface of synthesized LMS-NM adsorbent in the diameter

range of 500 to 800 μm were confirmed through BET analyses. Batch adsorption experiments and Langmuir adsorption isotherm showed a high adsorption capacity of chromate anion removal from water solutions (62.92, 66.91 and 70.75 mg g^{-1} at 25, 35 and 40 $^{\circ}\text{C}$, respectively). The analysis of the adsorption isotherms and thermodynamic parameters proved the adsorption being a spontaneous and endothermic process. This research indicates that the abundant and heavily underutilized kraft lignin, with the adequate functionalization, can be used as an economic and efficient bio-adsorbent with enhanced adsorption capacity for chromate anions and possess a significant industrial wastewater treatment potential.

4.1 Acknowledgement

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5 Nomenclature

LMS-NM –lignin microspheres, amino-modified and nanomagnetite functionalized
 BET – Brunauer, Emmett, Teller method
 FTIR – Furrier Transformation Infrared Spectroscopy
 LMS – Lignin microsphere adsorbent
 NM – Nanomagnetite particles
 pH_{PZC} – PH value at the point of zero-charge

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