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MODIFIED LIGNIN-BASED MICROSPHERES AS A GREEN SORBENT FOR THE REMOVAL OF CHROMIUM IONS

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Abstract

The unique chemical structure of lignin shows the possibility of its application as a basic material for the sorption of various pollutants from water. In this paper, the newly synthesized porous lignin-based material was used to remove Cr(VI) ions. Modified lignin microspheres (LMS) were synthesized by the process of inverse copolymerization of kraft lignin with poly (ethylene-imine), and amino modified iron oxide (magnetite) using epoxy-functionalized cross-linker. The shape of obtained adsorption material was partially spherical to spherical. The functionalization was performed to improve the pollutant removal capacity. Structural and surface characteristics of the LMS microspheres were characterized by Brunauer-Emmett-Teller method (BET), Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and point of zero charge pH (pH_{PZC}). The maximum adsorption capacity for oxyanion Cr(VI) was 77.024 mg g^{-1}obtained by Langmuir adsorption isotherm at 35°C. Based on kinetic studies, the adsorption process follows a pseudo second-order model. Thermodynamic parameters have shown that the adsorption process is endothermic and spontaneous. LMS is an environmentally friendly, cost-effective and therefore promising adsorbent for the removal of Cr(VI) with efficient adsorption and reusability.

Keywords: lignin-based sorbent, heavy metal removal, adsorption, wastewater treatment

INTRODUCTION

In recent years, a large amount of scientific research has been based on the use of natural materials to remove contaminants from polluted water. In order to eliminate them, several methods have been discovered, among which adsorption stands out as a very flexible, efficient and reliable method [1]. Heavy metal ions are stable, highly toxic and non-biodegradable pollutants. In order to make their removal more efficient and economical, the naturally available materials and nanoparticles are most often used as adsorbents, because of the developed specific surface, higher porosity and larger number of functional groups.

Natural lignocellulosic materials, which are cellulose, lignin and hemicellulose, are very popular because of their structure. Lignin, the second most abundant natural polymer besides cellulose, includes various structural groups including carboxyl and phenolic units. It is continuously researched in order for lignin to reach its full potential as an ecological bio-adsorbent for the efficient removal of pollutants from wastewater [2]. Chemical modifications made to the structure of lignin strengthen its affinity, resulting in improved miscibility with other polymer matrices, whereby composites of improved performance can be obtained [3].

The subject of this study is the synthesis of adsorption materials from kraft lignin, using the procedure of suspension copolymerization, followed by additional modification of the obtained material with iron oxide nanoparticles (magnetite). Thus, synthesized and chemically modified material was used to remove chromium oxyanion from water in the batch system.

MATERIALS AND METHODS

Materials

The following materials were used to optimize LMS microspheres and adsorption processes: chloropropane epoxy (Merck Schuchardt), kraft lignin (KL), liquid paraffin oil and poly (ethylene imine) grafting agent (PEI) (Sigma-Aldrich), sodium alginate (medium viscosity) and sodium lauryl sulphate (Centrohem). Iron (II)-chloride and iron (III)-chloride (Merck) were used for the synthesis of magnetite. The chromium solution (10 ppm) was made using a standard manufactured by Carl Roth Gmbh.

Preparation of adsorbent and adsorption experiments

Lignin microspheres were synthesized by the copolymerisation of lignin with PEI, amino modified magnetite in liquid paraffin/water suspension using chloropropane epoxy cross-linker. Sodium dodecyl benzenesulfonate and sodium 5 wt% alginate solution was used as emulsifier. The synthesis procedure is developed by Popovic *et al.* [4].

Evaluation of adsorption efficiency of Cr(VI) oxyanions on LMS were performed at temperatures of 25 °C, 35 °C, 45 °C with variation in sample weight (1, 2.5, 5, 7.5 and 10 mg) and contact time (5, 10, 15, 30 and 60 min) with continuous stirring. A volume of 10 ml of Cr(VI) solution with a concentration of C_i=10 mg L^{-1} and pH value 6 was used in order to determine the efficiency and define the optimal conditions for adsorption on LMS materials. The calculation of adsorption capacities was performed using the appropriate equation [5].

Material characterization

The synthesized sorbent was recorded using Fourier transform infrared spectrometry (FTIR) in order to examine present functional groups in obtained material. Nitrogen adsorption-desorption isotherms were determined using a Micromeritics ASAP 2020 instrument, while the specific surface area and the volume of the mesopores of the samples was calculated according to the Brunauer, Emmett, Teller (BET) method and Barrett, Joyner and Halenda (BJH) method, respectively. Morphology and composition of the sample surface was examined using TESCAN MIRA3 FEG electron microscope (SEM). Adsorption properties were determined performing equilibrium adsorption, kinetic and thermodynamic studies in the batch system following the Taguchi model. Ion concentration after adsorption was analyzed by inductively coupled plasma mass spectrometry (ICP-MS).

RESULTS AND DISCUSSION

Material characterizations

As can be seen from Figure 1a, the LMS sample is spherical in shape with irregular edges which can be explained by additional functionalization with magnetite nanoparticles. Moreover, high porous structure was obtained via magnetite functionalization of LMS (Figure 1b, Table 1).

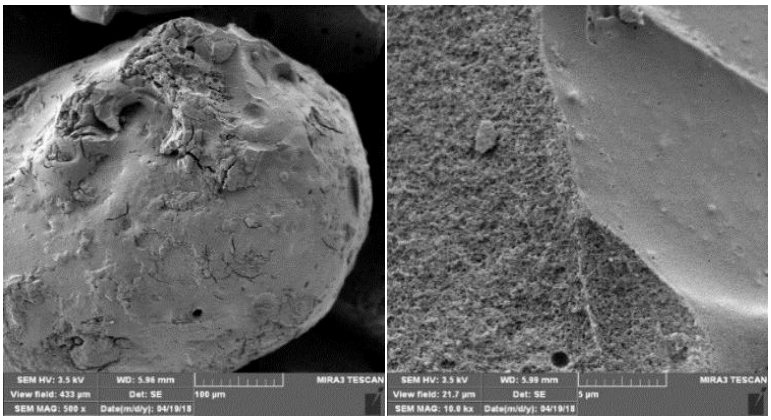

Figure 1 *SEM images of modified adsorbent at 100 and 10.000 magnifications*

Table 1 *Textural properties of modified LMS adsorbent*

Adsorbent	S_{BET}, m^2/g	V_{total}, mL/g	$V_{mesopore}$, mL/g	$D_{avmesopore}$, nm	D_{max}, nm
LMS	3.81	0.0228	0.0224	10.95	20.25

The values of 3.81 m^2 g^{-1} and 0.0228 mL g^{-1} for specific surface area and total pore volume, respectively, was determined while the mean pore diameter was 10.95 nm (Table 1). Results indicate that developed LMS represents a promising adsorbent for the removal of Cr(VI).

The FTIR spectra of modified lignin microspheres with magnetite are shown in Figure 2. The peaks recorded at 2930 and 2845 cm^{-1}, which is characteristic for symmetric and asymmetric C-H stretching vibrations of the methylene group [6]. Bands at wavelengths of 1728 cm^{-1} and 1459 cm^{-1} indicate the contribution of vibrations of the aromatic structure of lignin. The low-intensity peak at 1389 cm^{-1} can be attributed to the vibrations of the syringyl aromatic rings and the stretching C-O vibrations, while the vibration at 1250 cm^{-1} originates from the guaiacyl aromatic rings. The band at 1152 cm^{-1} originates from the deformation vibrations of C-O bonds in primary alcohol and phenolic groups [7] correspond to the successful copolymerization between lignin, PEI, amino functionalized magnetite and epoxy-chloropropane. Peaks at lower wavelengths are associated with deformation vibrations of C-H bonds in aromatic rings and bending vibrations of N-H bonds outside the plane (808 cm^{-1} and 781 cm^{-1}) [7,8]. The range between 530 and 781 cm^{-1} corresponds to the vibration of the Fe-O / Fe-OH magnetite phase [8].

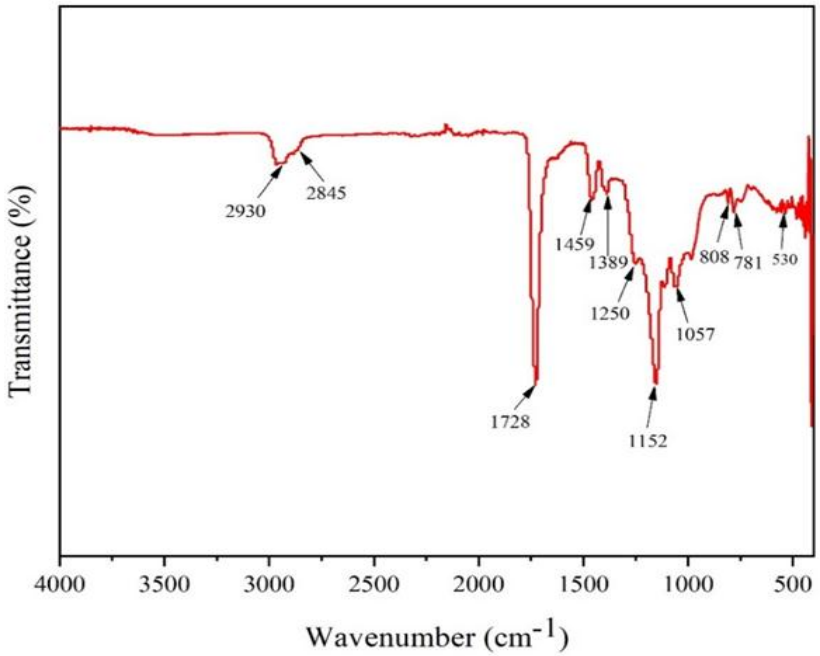

Figure 2 *FTIR spectrum of synthesized LMS-Fe_3O_4*

Adsorption kinetics

Pseudo-second-order (PSO) model was used to predict the law of kinetic rate. The results obtained by adjusting the experimental data with selected kinetic model show high match estimated according to the regression coefficient (R^2). The PSO model is given by equation (1) [9]:

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

Table 2 *The PSO kinetic parameters for Cr(VI) adsorption on LMS adsorbent (Ci=10.00 mg L^{-1}, pH=6, m/V=125 mg L^{-1}, T=25 °C)*

Adsorbent	Model parameters	Pseudo-second
LMS-Fe_3O_4	k (k_1, k_2) (g mg^{-1} min^{-1})	0.467
	R^2	0.998
	Ea	8.360

The results of the PSO model indicate the rapid mass transfer and the internal effect of diffusion within the particles on the total mass transport within the pore networks.

The state of interaction/binding of the adsorbate on the surface of the solution/adsorbent is described by adapting the experimental data to Langmuir and Freundlich adsorption isotherms. The rate constants from intra-particle diffusion model are given in Table 3. The adsorption capacities of LMS material increases with the temperature increase and the highest value was obtained at 35 ^oC (72.06 mg g^{-1}).

Table 3 *Results of isothermal models for the adsorption Cr(VI)*

Isotherm models and parameters		Temperature		
		25 °C	**35 °C**	**45 °C**
Langmuir isotherm	q_m (mg g^{-1})	64.72	68.49	72.06
	K_L(L mg^{-1})	0.14	0.15	0.16
	R^2	0.998	0.999	0.999
Freundlich isotherm	K_F (mg g^{-1}) (mL mg^{-1})$^{1/n}$	8.30	8.96	9.67
	1/n	0.65	0.71	0.71
	R^2	0.984	0.9844	0.983

Thermodynamic study

The influence of temperature on the adsorption process was investigated at three different temperatures. The obtained thermodynamic parameters are shown in Table 4.

Table 4 *Calculated thermodynamic parameters*

Adsorbent	ΔG^{Θ} (kJ mol^{-1})			ΔH^{Θ} (kJ mol^{-1})	ΔS^{Θ} (J mol^{-1} K^{-1})	R^2
	25 °C	**35 °C**	**45 °C**			
LMS-Fe_3O_4	-32.17	-33.12	-34.84	7.45	132.50	0.5371

Negative values of Gibbs free energy (ΔG°) at all temperatures indicate the spontaneity of the adsorption process which occurs via both physisorption and chemisorption mechanisms (32.17–34.84 kJ mol^{-1}). Positive values of enthalpy (ΔH°) and entropy change (ΔS°) indicate the endothermic nature of the sorption process, better stability of the complex and easier feasible adsorption process, as well.

CONCLUSION

In this paper, the lignin-based material was modified with amino-magnetite to improve the adsorption capacity of the spherical adsorbent to remove chromium oxyanions. The performed kinetic and thermodynamic studies have confirmed the high potential of this material as an adsorbent, as well as the nature of the adsorption process, spontaneity and endothermic binding of pollutants. FTIR and SEM analyses confirmed the structure of the modified LMS and provided information on the groups involved in chromium ion binding. The results of the PSO model indicate the rapid mass transfer and the internal effect of diffusion within the particles on the total mass transport within the pore networks. The presented methodology opens new guidelines in the field of environmental engineering, especially in the revaluation of industrial wastewater treatment.

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