ABSTRACT: Efficient and sustainable recycling of cobalt(II) is of increasing importance to support technological development in energy storage and electric vehicle industries. A composite material based on membrane-filtered lignin deposited on nanoporous silica microparticles was found to be an effective and sustainable sorbent for cobalt(II) removal. This bio-based sorbent exhibited a high sorption capacity, fast kinetics toward cobalt(II) adsorption, and good reusability. The adsorption capacity was 18 mg Co(II) per gram of dry adsorbent at room temperature (22 °C) at near-neutral pH, three times higher than that of the summarized capacity of lignin or silica starting materials. The kinetics study showed that 90 min is sufficient for effective cobalt(II) extraction by the composite sorbent. The pseudo-second-order kinetics and Freundlich isotherm models fitted well with experimentally obtained data and confirmed heterogeneity of adsorption sites. The promising potential of the lignin−silica composites for industrial applications in the cobalt recovering process was confirmed by high values of desorption in mildly acidic solutions.

INTRODUCTION

Lithium ion batteries (LIBs) are a key in enabling technology for battery electric vehicles (BEVs), energy storage, and mobile consumer electronic devices. Cobalt(II) is used in the cathodes of most batteries for BEVs and consumer electronics. As these technologies proliferate, it is anticipated that the global demand for cobalt(II) could soar to exceed the global supply.1,2 Presently, spent battery materials are largely sent to landfills, and the transition metal ions contained in this waste pose a concern as they are hazardous if leached to groundwater. Indeed, cobalt(II) can cause serious physiological damage to humans, including lung irritations, bone defects, or heart, liver, and thyroid damages. Allowable concentrations of cobalt(II) in irrigation water and livestock watering should not exceed 0.05 and 1 mg/L, respectively.3

To ameliorate the supply and environmental concerns surrounding the use of cobalt(II) in batteries, there is an increasing interest in the industry to improve recycling processes for battery materials. To meet this goal, the development of cobalt(II) recovery methods, which utilize cheap, sustainable materials, is highly desirable as cobalt(II) is one of the most valuable components of LIBs.1−4 An effective method for the removal of cobalt ions from aqueous solutions such as wastewaters is adsorption to insoluble substrates. Adsorption is regarded as highly efficient and does not require complicated procedures, i.e., adsorption can be carried out at near-neutral pH. Many materials have been already investigated as possible heavy metals ion sorbents, such as activated carbon, fly ash, biomass, zeolites, modified wood, modified cotton, lignin, peat, and so forth.5−12

Recently, various sorbents have been examined for cobalt adsorption from an aqueous solution. Ferri et al.13 have demonstrated adsorption of cobalt(II) on hydroxyapatite with a maximum sorption capacity of 22.5 mg/g. Zhuang and Wang14 obtained a maximum sorption capacity of 15.24 mg/g using a magnetic graphene oxide/chitosan composite as a sorbent. There has also been work carried out on cobalt(II) adsorption by using Si/Ti-based, amino-functionalized hybrids,15 graphite, activated carbon,16 or hydrogels.17 These investigations highlight the present interest in the development of new materials as sorbents for cobalt(II).

Among materials presently exploited as sorbents, silica-based materials are very promising. They feature a high surface area, which provides high adsorption capacity, low costs, and are prepared from abundant materials. To tailor the selectivity of
silica sorbents, it is possible to functionalize the surface of silica-based materials with materials rich in functional groups.18–21 Lignin, one of the most abundant biopolymers found in nature, features a range of coordinating functional groups, such as methoxyl, hydroxyl aliphatic and phenolic, carboxyl, and so forth,22 and is on its own an effective bio-based sorbent for aqueous solutions of heavy metal ions. Previous research has been focused on using lignins for adsorption of heavy metal ions, such as cobalt(II)10,23,24 mercury(II),10,23 cadmium(II),19–23 nickel(II),20,22,24 lead(II),18,21–23 silver(I),18 or copper(II),22,23,25 as well adsorption of arsenic,26 pesticides,22 and organic dyes.26 Besides the adsorption, lignin-based biomaterials find applications in plant protection, medicine, and biocatalysis.27

Modified lignin obtained as a byproduct during the paper production (Kraft process) is called kraft lignin, and it accounts for about 85% of total lignin production in the world.25,28 Kraft lignin not only has higher phenolic, hydroxyl, and carboxyl group contents than those in native or other technical lignins, but it also has different molecular weights and cross-linking densities.29,30 From an ecological point of view, it is important to use materials that can be obtained from sustainable sources. Hence, biomaterials, known since antiquity, are currently being investigated with a renewed interest.31 Several studies have been performed using silica–kraft lignin hybrid materials for adsorption of heavy metal ions20 and organic dyes.26 The synthetic methods to prepare such bio–inorganic hybrid materials are well described in the literature.28,32 Combining silica and kraft lignin results in hybrid materials typified by their high specific surface areas for adsorption and favorable physical properties, such as robust thermal stability and mechanical strength. Given the environmentally benign nature of these materials, it is envisioned that they will be favorable for large-scale processes.20

Herein, we disclose that a kraft lignin–silica composite is a highly efficacious sorbent for extraction of cobalt(II) from aqueous solutions. A detailed adsorption study elucidates the influence of different parameters, such as pH, time, and concentration, on the sorption processes. Several isotherm and kinetic models were applied to analyze the obtained experimental equilibrium data and to understand the mechanisms of adsorption and the rate-controlling step of the process. The possibility to recover and reuse the composite was demonstrated by conducting desorption tests.

## EXPERIMENTAL SECTION

### Materials

Kraft lignin (CleanFlowBlack, CleanFlow AB, Sweden) was obtained by ultrafiltration through a ceramic membrane with a cutoff of 5 kDa. The molecular weight of kraft lignin was ~3000 Da, and the contents of functional hydroxyl and carboxyl groups were 7.28 and 0.28 mmol/g, respectively.20 Cobalt(II) nitrate was purchased from VWR. All chemicals used were reagent grade.

### Synthesis of Lignin–Silica Hybrid Composites and Silica

Lignin–silica composites were obtained by the sol–gel method through silica precursor hydrolysis in an activated lignin solution by amino-contained silane. For comparison, silica was synthesized by the same method. Detailed synthesis procedures for composites and silica were developed and described in our previous synthetic work.20 In the current study, reproducibility and scaling of the sorbent were checked. For that, the synthesis was reproduced with the same initial reagent ratio and with a double-sized reaction batch.

### Methods: Transmission Electron Microscopy (TEM).

Five microliters of the composite suspension (approximate dose of 0.1 mg/mL) was deposited on a 200 mesh copper grid (Ted Pella Inc., USA; prod. no. 01800-F) and dried on air for 30 min. The TEM experiment was performed on a Hitachi HT7700 series instrument (Hitachi, Japan) at an accelerating voltage of 100.0 kV and emission current of 8.0 μA.

### Scanning Electron Microscopy (SEM).

Field-emission scanning electron microscopy (FE-SEM, S-4800, Hitachi, Japan) was applied.

Energy-dispersive X-ray spectroscopy (EDS) was performed on a TEM grid on a Hitachi field-emission S-4800 microscope with an EDS detector (Hitachi, Japan), at an accelerating voltage of 15 kV and emission current of 10.5 μA.

### Specific Surface Area and Pore Size Distributions.

The specific surface area and pore volume were determined from nitrogen adsorption/desorption isotherms at 77 K (Micromeritics ASAP 2020 sorption analyzer). The samples were degassed at 353 K before the measurements. The pore size distributions (PSD) were calculated using the nonlocal density functional theory (NLDFT) method with a model of cylindrical pores in silica and DFT with a self-consistent regularization procedure and models of slit-shaped and cylindrical pores and voids between particles in silica and silica/kraft lignin as described in the Supporting Information.

### SAXS.

Small-angle X-ray scattering (SAXS) analysis of the composite material was performed using an Empyrean (PANalytical, Netherlands) diffractometer with Cu Kα radiation (with a parallel beam X-ray mirror with W/Si crystal) using a transmission mode with scans over the 0.115–5° range with an increment of 0.01° at the continuous scan mode at 293 K under the procedure described in detail by Goliszew et al.33 More details are provided in the Supporting Information.

### Adsorption/Desorption Studies.

The adsorption isotherms for aqueous solutions of cobalt(II) were measured using a static method. The batch adsorption experiments were performed by shaking 0.05–0.07 g of the synthesized composite or initial kraft lignin or silica in flasks containing 25 mL of cobalt(II) solutions at different concentrations to study the extent of metal adsorption. The effect of the initial pH of the solution on the adsorption was studied using an initial cobalt(II) concentration of 10 mg/L and by adjusting the initial pH in a range of 1–10 using 0.1 M HCl (pH 1.1), 10% sodium acetate (pH 2.4), acetate buffer (pH 5.0), phosphate buffer (pH 7.0), ammonia acetate buffer (pH 8.0), borate buffer (pH 9.6) solutions, and deionized water. For performing the kinetic study, the initial cobalt(II) solutions with a concentration of 10 mg/L were shaken with the silica–kraft lignin composite, and the equilibrium concentrations were measured within 0.5–24 h. To evaluate the isotherms, the experiments were performed with a varying concentration of cobalt(II), ranging from 2 to 200 mg/L at 22, 40, and 60 °C. The flasks containing cobalt(II) solutions and the sorbent in a dose of 2.8 g/L were shaken for 1.5–3.0 h. For all adsorption experiments, an orbital shaker–incubator (Grant-bio, ES-20) was used, and the speed was adjusted to 180 rpm. After adsorption, the material was separated via filtration through a paper filter. Spectrophotometric determinations of cobalt(II) in the equilibrium aqueous phases were performed using a photometer (WPA, S800) with square cuvettes (optical path length l = 1 cm). The measurement was conducted at λ =
500 nm. The adsorbed amounts of substances were calculated using the equation

\[ q_e = \left( c_0 - c_e \right) \frac{V}{m} \]

where \( c_0 \) is the concentration of the initial solution, \( c_e \) is the equilibrium concentration of the metal ions, \( V \) is the volume of the equilibrium solution, and \( m \) is the mass of the applied sorbent.

The removal efficiency (\( R \)) was calculated using the formula

\[ R = \left( \frac{c_{ads}}{c_0} \right) \times 100\% = \left( \frac{c_0 - c}{c_0} \right) \times 100\% \]

where \( c_0 \) is the concentration of the metal ions in the initial solution, \( c_{ads} \) is the concentration of the adsorbed metal ions, and \( c \) is the equilibrium concentration of the metal ions in the aqueous phase.

The recovering ability of the sorbent was studied subsequently by using the following inorganic acids as eluting agents: 0.1 M HCl, 0.1 M H\(_2\)SO\(_4\), and 0.1 M HNO\(_3\). For cobalt(II) ion desorption determination, the appropriate amount of used sorbent was put into 25 mL of the eluting agent. The system was shaken at a rate of 180 rpm. After 90 or 60 min, the solution was separated from the sorbent by filtration. The desorption percentage (%) was calculated from the ratio of the quantity of adsorbed cobalt(II) to the quantity of desorbed cobalt(II) for each eluting agent.

## RESULTS AND DISCUSSION

**Sorbent Synthesis and Characterization.** Sol–gel synthesis of membrane-fractionated kraft lignin–silica was conducted through two-step synthesis as presented on Figure S1. Conducting the in situ formation of silica in the presence of a solution containing activated fractionated kraft lignin facilitates the formation of hybrid materials with strong bonds between the organic and inorganic phases.\(^{30}\) The formation of silica network and successful aminomethylation of lignin were confirmed by FTIR spectra and XPS analysis of synthesized hybrids in comparison with the initial lignin, silica, and aminomethylated lignin (Figure S2, Table S1, and Figure S3).\(^{30}\) In order to check the reproducibility of the developed hybrid composite and its potential for scaling up, the synthesis was conducted with a double-sized reaction batch. TGA analysis was applied in order to check and compare the reproducibility of the lignin % weight content in samples from the initial synthesis and after doubling of the reaction batch. TG and DTG curves of membrane-filtered kraft lignin–silica hybrids are presented in Figure S4. The % weight content of lignin was found to be 70.0% ± 2 for the batch reaction with the initial mass of lignin being 3 mg. For the scaled
experimental synthesis batch, the lignin content was found to be 73.0% ± 5.

**Textural Characteristics Study.** The surface morphology and textural characteristics of adsorbents play an important role in adsorption processes. Developed specific surface area and porosity are valuable characteristics of materials that provide accessibility to the functional groups within pores. The SAXS method (Figure 1, Figures S5 and S6) gives, in contrast to the adsorption methods, the total textural characteristics related to both open and closed pores (analyzed in the range of 0.2–250 nm in pore radius). Therefore, the textural characteristics values determined using the SAXS method could be much greater than those determined using the adsorption data (see the Supporting Information). This difference increases for strongly compacted materials composed of macromolecules or nanoparticles (with restricted possibility of penetration of adsorbed molecules into the inner space of the compacted structures). The SAXS occurs at a surface of each macromolecule in any cavity between neighboring macromolecules or functionalities as well as inner solid particles if they have closed pores inaccessible for adsorbed molecules.

Both the pore size distributions (Figures 1a and 2) and particle size distributions (Figure 1b) demonstrate that the majority corresponds to sizes smaller than 10 nm in radius. This relates to the structures with small silica nanoparticles compacted in globules as well as the lignin macromolecules bound to silica globules. These structures have values of $S_{SAXS} = 469$ and $536 \text{ m}^2 \text{g}^{-1}$, which are much greater than $S_{BET} = 195$ and $92 \text{ m}^2 \text{g}^{-1}$ for silica and silica/lignin, respectively. This is a consequence of silica nanoparticles and macromolecules being strongly compacted in both silica and composite microparticles, and nitrogen molecules can sense only a part of a surface accessible for $N_2$. The SAXS method, in contrast to nitrogen molecules adsorbed only onto accessible surface patches, senses the voids between the nanopores per se and macromolecules in the secondary structures and gives a larger total surface area (including both patches accessible and inaccessible for nitrogen molecules). The similarity in the nano/microstructure of silica particles in the studied materials leads to a similarity in the chord ($h$) size distributions (CSD, corresponding to thickness of uniform fragments in the micro/macrostuctures) at $h < 10$ nm (Figure S6). However, the CSD are different at $h > 10$ nm for the materials studied due to lignin contribution. Nitrogen adsorption and desorption isotherms for the silica and kraft lignin–silica (Figure S7) show that the hysteresis loop is open for silica alone in contrast to that of silica/lignin. Solid silica particles cannot swell in the nitrogen fluid (this effect can give the open hysteresis loop). Thus, pores in silica microparticles are not only narrow but also long and tortuous. The hysteresis loop for silica/lignin is closed because lignin strongly blocked entrances into silica pores (Figures 1a and 2). Lignin macromolecules form their own pores over a broad range of sizes, but the specific surface area $S_{BET}$ twice decreases in comparison to that of silica alone. However, the SAXS method gives a larger $S_{SAXS}$ value for the composite (Table S2) because macromolecules are less densely packed in the composite than silica nanoparticles in globules. One can assume that the porosity of the silica/lignin composite is enough for effective adsorption of metal cations because in the aqueous media, the polymer shells of silica particles could be less densely packed due to swelling in water and repulsive interactions between charged functional groups.

The pore size distributions (PSD) were calculated using nitrogen adsorption–desorption isotherms (recorded using a Micromeritics ASAP 2020 V4.04 adsorption analyzer, Figure S7). The nonlocal density functional theory (NLDFT) using a model of cylindrical pores in silica (Figure 2a) and DFT with a self-consistent regularization procedure (SCR) and slit-shaped pores and voids between polymer particles and cylindrical pores in silica (SCV) (Figure 2b) are described in detail elsewhere.\(^1\)\(^-\)\(^2\)\(^,\)\(^1\)\(^3\)\(^,\)\(^3\)\(^5\)\(^,\)\(^3\)\(^8\) For a better view of the PSD at large values of $R$, the differential PSD with respect to the pore volume $f_v(R) \approx dV/dR$, $\int f_v(R)dR \approx V_p$ could be recalculated to incremental PSD (IPSD) at $\Phi_v(R_i) = \int (f_v(R_i) + f_v(R)) (R_{i+1} - R_i)/2$ at $\sum \Phi_v(R_i) = V_p$ (Figure 2b).

From TEM micrographs of kraft lignin–silica, the ordered structure of silica could be seen (Figure 3). SEM-EDS revealed sulfur signals that corresponded to SiO$_2$, silicon and lignin carbon distributed evenly in hybrid composite particles. Equal distribution of sulfur from mercapto groups of kraft lignin and nitrogen from applied aminosilane additionally confirmed homogeneous distribution of lignin in the obtained material as...
well as successful aminomethylation on the first step of the synthesis (Figure 4).

**Adsorption Kinetics of Cobalt(II).** The kinetics study was conducted in order to determine the adsorption rate, adsorption mechanism, and the influence of contact time between the adsorbent and adsorbate on the adsorption process. A cobalt(II) solution with an initial concentration of 10 mg/L was applied in neutral aqueous media. The influence of phase contact time onto Co(II) adsorption by the silica–kraft lignin composite is presented on Figure S8. The results indicate that the equilibrium state was established within 1.5 h of contact time. The higher removal efficiency during a time less than 1.5 h could be a result of diffusion of metal ions into micropores of the composite. It was found that after equilibrium, there is removal of 63% of cobalt(II) from the solution. By comparison to previously reported sorbents for Co(II), it is evident that lignin–silica is comparable to the most effective polymer-based and organic–inorganic sorbents.26,32

Kinetic models were applied in order to describe changes in the concentration of adsorbate as a function of time were used until equilibrium was reached. This enables to study the adsorption mechanisms and rate-controlling steps of the process in detail. The kinetics of the adsorption of cobalt(II) ions onto the silica–kraft lignin sorbent was studied using a pseudo-first-order kinetic model developed by Lagergren, a pseudo-second-order model by Ho and McKay,36 and an intraparticle diffusion model by Weber and Morris.37

The pseudo-first-order equation is given as

\[ \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \]

and the pseudo-second-order equation is given as

\[ \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]

where \( q_e \) and \( q_t \) are the amounts of Co(II) adsorbed (mg/g) at the equilibrium time and at any instant of time \( t \), respectively, \( k_1 \) (1/min) is the rate constant of the pseudo-first-order adsorption, and \( k_2 \) (g/mg/min) is the pseudo-second-order rate constant.

The kinetics data obtained were used to understand the possibility of the process of intraparticle diffusion. For this purpose, the Weber and Morris equation37 was used

\[ q_t = K_{IPD}^{0.5} + C \]

where \( K_{IPD} \) is the intraparticle diffusion rate (mg/min\(^{0.5}\)), and \( C \) is a constant.

The parameter values (Table 1) are summarized from fitting the experimental data with the applied kinetic models. As seen from the plots and correlation coefficients \((R^2)\), the pseudo-second-order equation kinetic model does fit Co(II) adsorption onto the silica–kraft lignin composite. The coefficient \( R^2 \) values were 0.330, 0.999, and 0.553 for the pseudo-first-order, the pseudo-second-order, and the intraparticle diffusion mechanism models, respectively. In our previous study devoted to Co(II) adsorption onto the silica–kraft lignin surface, the same relations were found.26

The linear relationship of \( t/q_t \) versus \( t \) from the constructed plot (Figure S5a,b) validated the pseudo-second-order equation as a useful model for the adsorption kinetics of Co(II) onto the silica–kraft lignin sorbent. The equilibrium sorption capacities \((q_{e,cal})\) and the pseudo-second-order rate constants \((k_2)\) were determined from the slope and intercept of the plot \( t/q_t \) versus \( t \). The adsorption rate was found to be relatively high at 7.677 g/mg-min compared to the results of dye adsorption by the same composite where the rate was in a lower range.
range of 0.015–0.02 g/mg·min. Such a high rate could be explained by higher affinity of a surface to the cobalt(II) cations and by higher accessibility of adsorption sites for metal ions than that for the larger dye molecules. Another explanation is a different mechanism; as for dye adsorption, it was a set of possible mechanisms: electrostatic interactions, hydrogen bonding, and π–π interactions, but for Co(II) ions, probable coordination by Lig–O is taking place. The calculated adsorption capacity values (Table 1) matched well with the experimentally obtained values.

The impact of the intraparticle diffusion mechanism on cobalt(II) adsorption onto the silica–kraft lignin composite was determined using the intraparticle diffusion model. It could be seen from Figure S5c that the plot $q_t$ versus $t^{0.5}$ is linear, which confirms that the diffusion controls the mass transfer rate. From the linearity of the plot $q_t$ versus $t^{0.5}$, the constant $C$ and the intraparticle diffusion rate $K_{IPD}$ were calculated. The constant $C$ was found to be larger than zero, indicating that the cobalt(II) adsorption can be affected by the boundary layer diffusion to a certain extent. The determination coefficient was found to be 0.11 for the silica–kraft lignin composite. The obtained results based on the kinetics study are in line with previously published data concerning the adsorption of bivalent heavy metal ions.

Figure 5. (a) Isotherms of cobalt(II) adsorption onto silica–kraft lignin at 22–60 °C, fitting with (b) Langmuir, (c) Freundlich, and (d) Temkin isotherm models.

Figure 6. Comparison of (a) adsorption capacity of silica–kraft lignin toward cobalt(II) at 22–60 °C and (b) adsorption capacity of the silica and kraft lignin alone and composite.
Adsorption Equilibrium. The cobalt(II) adsorption isotherms in the neutral media at room temperature (22 °C) and at increased temperatures up to 40 and 60 °C are presented in Figure 5a. The highest sorption of cobalt(II) was observed at the lowest temperature (22 °C). With an increasing temperature toward 60 °C, the adsorption capacity decreased by 75% (Figure 6a). Experimental adsorption capacities for the studied composite were 17.9 mg/g (0.30 mmol/g) at 22 °C, 14.5 mg/g (0.25 mmol/g) at 40 °C, and 4.7 mg/g (0.08 mmol/g) at 60 °C. Distribution coefficients calculated from the experimentally obtained data were found to be relatively high for isotherms in all temperature range: 1.14 L/g for 22 °C, 0.91 L/g for 40 °C, and 1.0 L/g for 60 °C. Taking into account the % weight of kraft lignin in the composite (70% ± 2) and that the lignin’s functionality playing a major role in cobalt(II) adsorption, the capacity of immobilized lignin was calculated and found to be 25.6 mg/g (Figure 6a).

The Co(II) adsorption onto pure silica and kraft lignin showed that the capacity of the composite is three times larger than the sum of the capacities of initial components alone: at 22 °C, the capacities of pure silica and kraft lignin were 3.37 and 2.52 mg/g, respectively, whereas for the composite it is 17.9 mg/g (Figure 6b). The same effect was observed for adsorption of methylene blue by the silica–kraft lignin composite in a previous study,26 which is additional adsorption of methylene blue by the silica–kraft lignin composite in a previous study,26 which is additional adsorption sites for ions and molecules adsorbed.

The Langmuir, Freundlich, and Temkin isotherm models were applied to analyze the obtained data. The linear form of the Langmuir model can be expressed as:

\[
\frac{c_e}{q_e} = \frac{c}{q_0} + \frac{1}{q_0 K_L},
\]

where \(c_e\) is the equilibrium concentration of ions (mg/L), \(q_e\) is the amount of the adsorbed ions (mg/g), and \(q_0\) and \(K_L\) are the Langmuir constants related to the adsorption capacity (mg/g) and the equilibrium constant (L/mg), respectively.

The sorption equilibrium data was also applied to the Freundlich model:

\[
\log q_e = \log K_f + \frac{1}{n} \log c_e,
\]

where \(K_f\) and \(n\) are the Freundlich constants related to the sorption capacity and sorption intensity, respectively.

The Temkin model of isotherm can be expressed as follows:

\[
c_e = \frac{RT}{b_T} \ln(K_T) + \frac{RT}{b_T} \ln c_{eq}
\]

where \(c_e\) is the concentration of ions in the solid phase (mol/g), \(b_T\) is the heat of adsorption (J/mol), \(K_T\) is the model constant (L/g), \(R\) is the gas constant (8.314 J/mol·K), \(T\) represents the absolute temperature (K), and \(c_{eq}\) denotes the equilibrium concentration of ions (mol/L) in the aqueous phase.

The characteristic parameters of each isotherm model were determined and summarized in Table 2. According to high correlation coefficients (\(R^2 = 0.99\)) obtained through application of the Langmuir isotherm model, one could assume good fitting of this model to experimental data (Figure 6b–d). The Langmuir isotherm assumes monolayer adsorption and is commonly used for description of the uptake on a homogeneous surface by monolayer adsorption with no interactions between the adsorbed ions. Through application of the Langmuir isotherm model, the capacity of the monolayer (\(q_m\)) at each applied temperature was calculated (Table 2). Thus, the \(q_m\) for silica–kraft lignin were found to be 18.35, 15.20, and 4.79 mg/g at 22, 40, and 60 °C, respectively. It was found that the adsorption of cobalt(II) onto the surface of the studied composite was favorable according to the values of \(K_w\), which were between 0 and 1.

The correlation coefficient for the Freundlich isotherm model was found to be relatively high for isotherms at 22 and 40 °C. In general, the Freundlich model is applicable to multilayer adsorption where non-uniform distribution of adsorption heat and affinities occurred over the heterogeneous surface. The heterogeneity of the composite surface could be explained by the set of functional groups corresponding to kraft lignin (hydroxyl and carboxyl groups) and hydroxyl groups of silica. In a previous work,40 the Freundlich isotherm was successfully used for describing heterogeneous systems of organic compounds or highly interactive species.

Based on the Temkin isotherm model, the heat of adsorption of cobalt(II) ions onto the silica–kraft lignin composite increased from 0.82 to 2.83 kJ/mol with the temperature increasing from 22 to 60 °C. The maximum binding energy for interactions between the composite surface and cobalt metal ions (\(K_T\)) was observed at 60 °C and was found to be 4.600 L/g.

The thermodynamic parameters: Gibb’s free energy change (\(\Delta G^0\)), enthalpy change (\(\Delta H^0\)), and entropy change (\(\Delta S^0\)) for the adsorption process were calculated from the following equations:

\[
\Delta G^0 = -RT \ln K_w
\]

and

\[
\Delta G^0 = \Delta H^0 - T \Delta S^0
\]

where \(R\) is the universal gas constant (8.314 J mol\(^{-1}\) K\(^{-1}\)), and \(T\) is the absolute temperature in K.

The negative values of \(\Delta G^0\) were –11.3, –11.9, and –16.4 kJ mol\(^{-1}\) for 22, 40, and 60 °C, respectively, confirm the feasibility of the process and the spontaneous nature of the adsorption. The \(\Delta H^0\) (30.23 kJ mol\(^{-1}\)) and \(\Delta S^0\) (–0.1384 kJ mol\(^{-1}\) K\(^{-1}\)) were obtained from the intercept and slope of the linear plot of Gibb’s free energy change versus temperature.

### Table 2. Isotherm Model Parameters Obtained for Co(II) Ion Adsorption onto the Silica–Kraft Lignin Sorbent

| Isotherm Model | 22 °C | 40 °C | 60 °C |
|----------------|-------|-------|-------|
| \(q_m\) mg/g  | 18.55 | 15.20 | 4.79  |
| \(K_w\), L/mg  | 0.098 | 0.095 | 0.379 |
| \(R^2\)        | 0.9908 | 0.9909 | 0.9908 |
| Freundlich     |       |       |       |
| \(K_w\), mg/g  | 1.60  | 1.49  | 1.17  |
| \(1/n\)        | 0.529 | 0.530 | 0.480 |
| \(R^2\)        | 0.9564 | 0.9418 | 0.7994 |
| Temkin         |       |       |       |
| \(b_T\), kJ/mol | 0.82  | 1.02  | 2.83  |
| \(K_T\)        | 1.906 | 2.026 | 4.600 |
| \(R^2\)        | 0.9528 | 0.9741 | 0.9258 |
Influence of Initial pH on Adsorption. As medium acidity is a crucial parameter for the adsorption process, the influence of initial pH onto Co(II) ion adsorption efficiency was investigated. The comparison of removal efficiency of Co(II) from solutions with an initial metal concentration of 10 mg/L onto the silica–kraft lignin composite as a function of the medium acidity is presented on Figure S10. It can be seen that 63% of cobalt(II) could be adsorbed on the composite surface from deionized water when cobalt(II) exists in the form of aqua complexes $[\text{Co(H}_2\text{O)}_n\text{]}^{2+}$ where $n = 4$ or 6. The highest cobalt(II) removal was found at pH 9.6 in the borate buffer. However, it should be taken into account that at these conditions, the equilibrium between “$\text{Co(OH)}(\text{H}_2\text{O})_n$” and $[\text{Co(H}_2\text{O)}_n\text{]}^{2+}$ is shifted toward $\text{Co(OH)}(\text{H}_2\text{O})_n^-$ as the initial concentration of cobalt(II) is higher than 3.5 mg/L. The degree of adsorption was 15% at pH 8.0 (in the ammonia acetate buffer) where cobalt(II) exists in the form of $[\text{Co(NH}_3)_n\text{]}^{2+}$ and $[\text{Co(NH}_3)_m\text{]}^{2+}$ ammonia complexes. It was found that the Co(II) adsorption is not effective at strong (pH 1.3 and pH 2.4) and slightly acidic media (pH 5.0), as well as at pH 7.0 (in the phosphate buffer). Thus, the synthesized composite showed a higher degree of sorption at pH $\geq 7$, which is in line with determined pH$_{pzc} = 6.3$ of the kraft lignin–silica surface (Figure S11).

Regeneration of the Adsorbent. For the desorption tests, 0.1 M solutions of inorganic acids HCl, HNO$_3$, and H$_2$SO$_4$ were used. As seen from the diagram (Figure 7), up to 48% of adsorbed cobalt(II) could be removed in a strong acidic medium (pH 1.4) in over 90 min. Due to the nature of background anions playing a role in the desorption process, nitric acid was found to be the most effective eluent for cobalt(II) desorption. By contrast, substantially lower cobalt recovery was observed when using 0.1 M HCl (20%) at pH 1.26 and H$_2$SO$_4$ (31.8%) at pH 1.21 as eluents. The results led us to conclude that silica–kraft lignin could be recovered and applied for next adsorption cycles. The relatively high Co(II) desorption in the acidic medium could be caused by breaking of coordination bonds at low pH, corresponding to protonation of carboxyl moieties.

As the highest adsorption was assumed at pH close to neutral and desorption was successfully acquired at the media with low pH, it could be assumed that the complexation is the main mechanism of Co(II) ions binding to the kraft lignin–silica surface. However, additional investigations are needed for the conclusion about the impact of hydroxyl groups of lignin or silica as well as carboxyl groups of lignin to the adsorption process.

In order to investigate the possibility of regeneration of the sorbent and its activity after continuous usage, adsorption–desorption of cobalt(II) was conducted in cycles. It was found that the kraft lignin–silica sorbent could be applied for two adsorption–desorption cycles with 0.1 M nitric acid as the most promising eluent among other tested inorganic acids. As it could be seen from Figure 8, the sorbent successfully regenerated after the first cycle, but regeneration ability decreased drastically during the second cycle.

![Figure 7. Desorption of Co(II) from used sorbents (1.5 h, 22 °C).](image-url)

![Figure 8. Desorption of cobalt(II) ions with two adsorption/desorption cycles of cobalt(II) ions (1 h, 22 °C).](image-url)

CONCLUSIONS

We have demonstrated that composites based on an inorganic support (nanoporous silica gel) and functional biomacromolecules (kraft lignin) are prosperous materials for sustainable metals recovering under mild conditions. The results showed that combination of kraft lignin and silica gel results in strong synergistic effects toward cobalt(II) removal. The combination of kraft lignin and silica leads to adsorption of 18 mg of cobalt(II) per gram of dry composite, while pure kraft lignin and silica alone showed three times lower adsorption capacity toward cobalt(II) of 3 mg/g for both ones. It was found that the silica–kraft lignin composite is characterized by fast Co(II) adsorption kinetics; equilibria were reached in 90 min of contact of aqueous and solid phases. Significant desorption of cobalt(II) from the composite surface (upon change in the media) yields the opportunity to recover and reuse the bio-based sorbent. As this composite is reusable and prepared under benign conditions from abundant materials, it can be considered as a green material. Presently, we are investigating this silica–kraft lignin composite as an adsorbent for metals from spent lithium batteries and will report these findings in due course.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c00492.

Small-angle X-ray scattering (SAXS), nitrogen adsorption–desorption isotherms for the silica and kraft lignin–silica composite, influence of phase contact time on the cobalt(II) adsorption, pseudo-first- and
pseudo-second-order plots, intraparticle diffusion plots for cobalt(II) adsorption kinetics onto the kraft lignin—silica composite, and influence of pH on the cobalt(II) adsorption onto the kraft lignin—silica sorbent at 22 °C (PDF)

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Notes
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