Co-precipitative preparation of sulfonated cellulose- magnetite hybrid sorbent for the removal of Cu$^{2+}$ ions

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Abstract

Novel sulfonated cellulose – magnetite (Fe₃O₄) composite sorbent was prepared and applied for the removal of Cu²⁺ ions from aqueous solution. It was characterized by infrared spectroscopy, X-ray fluorescence, elemental analysis, SEM, VSM and X-ray photoelectron spectroscopy. The effect sorbent dose, initial solution pH, temperature on the Cu²⁺ removal were studied. Removal of Cu²⁺ completed in 15 min and the sorption kinetics of Cu²⁺ is found to follow a pseudo-second-order kinetic model. Equilibrium test demonstrated that sorption of Cu²⁺ onto hybrid sorbent agreed well to the Langmuir adsorption model with a maximum adsorption capacity of 4.2 mg/g. Moreover, the optimum pH for Cu²⁺ removal found as ≥ 4. Furthermore, thermodynamic parameters reveal the feasibility, spontaneity and endothermic nature of the sorption process. In addition, Cu²⁺ ions can be desorbed from the sorbent with a 0.5 M H₂SO₄ solution.

Keywords: Cellulose, Copper, Hybrid sorbent, Magnetite, Sulfonation
Introduction

Because of their toxic effect on human health, there is a great concern on heavy metal concentration in water sources. Heavy metals such as Cu\(^{2+}\) are non-biodegradable in the environment, which even in trace amount can accumulate in living organisms through food chains\(^1\). It is well known that copper is a widely used material in the industry, which leads to many actual or potential sources of copper pollution\(^2\). Copper is one of the essential nutrients to humans and other life forms, however, at high concentrations, it is known to be one of the most toxic metal ions to living organisms\(^3\). The fate of elemental copper in water is complex and influenced by pH, dissolved oxygen and the presence of oxidizing agents and chelating compounds or ions.

World Health Organization (WHO) set its provisional guideline value of 2 mg/liter in drinking water\(^4\). Various technologies exist for the removal of metal ions which include filtration, chemical precipitation, ion exchange, adsorption, and membrane process\(^5\). Out of all such methods, several research studies have been conducted globally on natural polymers and its composites for the treatment of contaminated water and wastewater.

Cellulose is the most common natural raw material on earth and it has many benefits, such as low cost, biodegradability, and renewability. More importantly, cellulose is harmless to the environment, as it can easily return to the natural carbon cycle by the decay process of some decomposers\(^6\). In recent years, composite adsorbents that prepared by magnetite and natural polymers have attracted much attention due to its simplicity and easy separation. Combining the natural polymers with the magnetite avails the separation using an external magnetic field, good dispersion in water and recoverability\(^7\).

In this work, cellulose was modified with sulfonyl acid groups and then it was co-precipitated with magnetite to have hybrid sorbent, which has magnetic property. The chemical structure of cellulose-based sorbent was analyzed by infrared spectroscopy (IR), X-ray fluorescence (XRF),
elemental analysis and X-ray photoelectron spectroscopy (XPS). Batch adsorption experiments were performed to investigate the sorption behavior of the hybrid sorbent in relation to initial solution pH, sorbent dosage, contact time, initial Cu\(^{2+}\) concentration and temperature. The sorption kinetics, isotherms, thermodynamics, and regeneration of the sorbent were also studied in detail.

**Experimental**

*Reagents and chemicals*

The Sodium periodate (NaIO\(_4\), Acros Organics) and Sodium metabisulfite (Na\(_2\)S\(_2\)O\(_5\), Merck) used in the oxidation and sulfonation of cellulose. Ferric chloride (Fe(Cl)\(_3\).6H\(_2\)O) and Ammonium ferrous sulfate ((NH\(_4\))\(_2\)Fe(SO\(_4\))\(_2\).6H\(_2\)O, Merck) was used for the preparation of magnetite particles. Cellulose raw material was obtained from Denkim Kimya A. Ş. (Denizli, Turkey) and used without modification or treatment. HCl, H\(_2\)SO\(_4\), and NaOH obtained from Merck and used for the adjustment of solution pH and dissolution of iron salts.

*Preparation of sulfonated cellulose*

Sulfonated cellulose prepared as explained before. Briefly, 12 g of cellulose was transferred to 0.038 M 250 mL of NaIO\(_4\) solution and this mixture was stirred at 55 °C for 2 hours. Oxidized cellulose was filtered and washed with pure water then it was reacted with 0.242 M 250 mL Na\(_2\)S\(_2\)O\(_5\) (pH 4.3) for 3 hours at 60 °C. After this time, sulfonated cellulose was washed with pure water.

*Preparation of composite magnetite-sulfonated cellulose sorbent*

Experimental conditions for the preparation of magnetite was the same as explained in. The 23.3484 g FeCl\(_3\).6H\(_2\)O and 16.9404 g (NH\(_4\))\(_2\)Fe(SO\(_4\))\(_2\).6H\(_2\)O were each dissolved in 200 mL of acidified water (HCl and H\(_2\)SO\(_4\) were used for the acidification of solution), combined, and nitrogen was introduced into the solution. The resulting Fe\(^{2+}\)/Fe\(^{3+}\) solution was transferred to sulfonated cellulose containing beaker and nitrogen gas passed through this mixture for 15
minutes. The obtained mixture was added into 1000 mL of 2M of NaOH solution under nitrogen gas with vigorous stirring at 80°C. The obtained black composite particles were separated from the reaction medium by applying a magnetic field and washed with ultrapure water until the pH was less than or equal to 8. The prepared sorbent was dried in the oven then ground and used in the experiments.

**Characterization of sorbent**

Infrared spectra of sorbent as KBr pellets were obtained using a PerkinElmer Fourier transform spectrometer (One-B model). Compositional analysis of the prepared sorbent was carried out by using X-ray fluorescence (Spectro Xepos, Ametec), Leco Truspec CHN-S elemental analyzer and X-Ray Photoelectron Spectroscopy (XPS). The morphology of the prepared sulfonated cellulose and hybrid sorbent were analyzed by scanning electron microscopy (SEM) (Thermo scientific, Apreo S LoVac, USA). Magnetization curve was provided at room temperature using vibrating sample magnetometer (VSM, 7300, Lakeshore) under a magnetic field up to 10 kOe.

**Batch sorption experiments**

A series of batch sorption experiments was applied to investigate the optimum sorption parameters for Cu²⁺ removal. Experimental conditions for such parameters were summarized in Table 1. Batch experiments were performed at least twice (except kinetic experiment) and averaged experimental results are given. The determination of Cu²⁺ was performed using an atomic absorption spectrometer (Varian SpectrAA 220 model) at a wavelength of 324.7 nm.

The percent removal (R, %) of Cu²⁺ was calculated with Eqn. 1 and capacity of sorbent (q as mg-Cu/g-sorbent) was calculated with Eqn.2.⁹

\[
R(\%) = \frac{c_0 - c_e}{c_0} \times 100
\]

………………. (1)
In these equations, \( C_0 \) is the initial \( \text{Cu}^{2+} \) concentration (mg/L) \( C_e \) is the \( \text{Cu}^{2+} \) concentration in the solution after sorption experiment (mg/L). \( V \) is the volume of solution (L) and \( m \) is the mass of the sorbent (g).

\[
q = \frac{(C_0 - C_e)V}{m} \tag{2}
\]

Results and Discussion

Characterization of sorbent

In order to clarify the structure of composite sorbent, the IR, elemental analysis, and XPS, SEM and VSM techniques were used. Figure S1a, S1b and S1c shows the SEM images of sulfonated cellulose and magnetite-sulfonated cellulose hybrid sorbent. As can be seen from the Figure S1a sulfonated cellulose has a fiber shape. The magnetite particles are deposited on the sulfonated cellulose (S1b) and the average length of the hybrid sorbent is 250 µm (Figure S1c).

Magnetic hysteresis loops of the bare magnetite and hybrid sorbent were investigated by VSM at room temperature. Figure 1 shows the magnetization curves of bare magnetite and the hybrid sorbent. The magnetite reached a saturation magnetization value (\( M_s \)) of 53.7 emu/g while the \( M_s \) value of the hybrid sorbent is reduced to 26.3 emu/g which is due to contribution of non-magnetic sulfonated cellulose to the total mass of the hybrid sorbent.

Infrared spectra of the prepared sorbent is depicted in Figure S2. Three main absorption band of the sample at 3415 cm\(^{-1}\) corresponding to OH stretching vibrations in cellulose molecules, whereas peak obtained at 2903 cm\(^{-1}\) refers to the CH\(_2\) and C–H stretching vibrations. The absorption peaks at 1423, 1159, 1116, 1056 and 896 cm\(^{-1}\) related to the CH\(_2\) symmetric scissoring in the pyranoid ring, C–O antisymmetric bridge stretching, and the crystal absorption...
peak of cellulose, C–O–C pyranoid ring skeletal vibration and the β-glycosidic linkages, respectively. The prominent peaks at 582 and 631 cm\(^{-1}\) are ascribed to stretching vibrations of Fe–O–Fe in Fe\(_3\)O\(_4\)\(^{5,8,10-12}\).

Such peaks clearly confirmed that prepared sorbent contains both sulfonated cellulose and magnetite. Table 2 gives the elemental compositions of prepared composite sorbent as obtained from XRF and elemental analysis.

Table 2 gives the elemental compositions of prepared composite sorbent as obtained from XRF and elemental analysis.

The prepared sorbent contains inorganic (magnetite) and organic (cellulosic) components. The amount of reactants (Fe\(^{3+}\), Fe\(^{2+}\) and sulfonated cellulose) was adjusted as to have composite sorbent with 1:1 mass ratio (magnetite: sulfonated cellulose). It can be seen from Table 2 that 54% of sorbent is inorganic (as Fe\(_2\)O\(_3\)) and 46% of sorbent is organic substituent, which is close to our expected mass ratio. This result is another evidence that sorbent has organic and magnetite component.

The Fe 2p XPS spectrum of composite sorbent is shown in Figure 2. Two main peaks at 710.38 (Fe 2p\(_{3/2}\)) and 723.96 (Fe 2p\(_{1/2}\)) which are the characteristic peaks of magnetite indicate that magnetite is present in composite sorbent\(^{13,14}\).

Effect of sorbent dose on Cu\(^{2+}\) removal

The effect of sorbent dose on the removal of Cu\(^{2+}\) ion is shown in Figure 3. It was observed from the figure that, removal of Cu\(^{2+}\) increased from 52% to >99% with an increase in sorbent amount from 0.025 to 0.2 g. The increase in the removal percentage with increment in sorbent dose is due to increase active sites on the prepared sorbent\(^{5,15}\). The 0.2 g sorbent dose found as optimum and used in subsequent experiments.
Effect of solution pH

Figure 4 shows the effect of the initial solution pH on the removal of Cu$^{2+}$ ion by the composite sorbent. Solution pH has an effect on Cu$^{2+}$ removal. At pH 1 and 2 sorbent could not remove Cu$^{2+}$ from solution but when the solution pH was increased a large increment on Cu$^{2+}$ removal was observed and pH between 4 and 9, 99% of Cu$^{2+}$ sorbed by the sorbent. There is an ion exchange reaction between the sulfonic acid group of sorbent and Cu$^{2+}$ ion as shown in Eqn. 3.

$$2 \text{Sorbent} - (SO_3^-Na^+) + Cu^{2+} \leftrightarrow \text{Sorbent} - (SO_3^-)2Cu^{2+} + 2H^+ \quad \text{........... (3)}$$

There is an electrostatic interaction between the sulfonic acid group (-SO$_3$Na$^+$) of the sorbent and Cu$^{2+}$ ions, which is non-specific. Same interaction also exists between H$^+$ ions and sulfonic acid groups. At low pH range, the concentration of H$^+$ ion is larger than Cu$^{2+}$ and if the concentration is increased in a series of experiments where all the other conditions are kept unchanged, the rate of exchange increases linearly with concentration thus H$^+$ ions sorbed at low pH values. The ion exchange reaction between the sulfonic acid group and H$^+$ is shown in Eqn. 4.

$$\text{Sorbent} - (SO_3^-Na^+) + H^+ \leftrightarrow \text{Sorbent} - (SO_3^-H^+) + Na^+ \quad \text{........... (4)}$$

When the initial solution pH was increased (H$^+$ concentration decreased), Cu$^{2+}$ ions sorbed by sorbent as shown in equation 3. As can be seen from Figure 4 that, optimum pH found as pH ≥ 4 for Cu$^{2+}$ removal.

Kinetic of the composite sorbent
The influence of contact time on the sorption of Cu\textsuperscript{2+} by the prepared sorbent is illustrated in Figure 5.

Kinetic of the composite sorbent is quite fast and in one minute 95% of Cu\textsuperscript{2+} removed from the solution and after 15 minutes removal rate reached the maximum (> 99%). The experimental results were also evaluated by using the most common kinetic models, which are pseudo first order and second order reaction model. The linear form of the pseudo first-order rate equation was given by following Eqn. 5.

\[
\log(q_e - q) = \log(q_e) - \frac{k_1 t}{2.303} \quad \text{................. (5)}
\]

Pseudo-second order kinetic rate equation is expressed as Eqn.6 \textsuperscript{19,20}.

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad \text{.................... (6)}
\]

The calculated parameters are summarized in Table 3

The correlation coefficient \(R^2\) for the pseudo-second-order model has a higher value (>99%) than the pseudo-first-order model. Obtained results indicate that the pseudo-second-order kinetics model is more desirable to interpret the sorption behavior of Cu\textsuperscript{2+} onto composite sorbent. The rate constant \(k_2\) found as 26.7 g/mg min. The value is in agreement with the short equilibrium times. The kinetic of prepared sorbent is compared with other sorbents given in the literature and results are summarized in Table 4. As can be seen from the table, prepared sorbent has relatively fast kinetic compared to other sorbents.
Sorption isotherm of Cu$^{2+}$ ion

The equilibrium isotherms for the sorption of Cu$^{2+}$ ions by composite sorbent is shown in Figure 6. As can be seen from the figure that, the capacity of sorbent increased with initial Cu$^{2+}$ concentration increment and then it reached the plateau. Ions are transported by conventional and molecular diffusional processes under the influence of concentration gradients (or strictly thermodynamic chemical potential gradients). Chemical potential can be written as shown in Eqn 7.

\[
\mu = \mu^0 + RT \ln \alpha 
\]  

Where \( \mu \) is the chemical potential, \( \mu^0 \) is the standard chemical potential and \( \alpha \) is the activity of ion.

Activity can be written as shown in Eqn 8.

\[
\alpha = f \chi C 
\]  

As shown in the equation in Eqn. 8, the activity of an ion is linearly proportional with its concentration thus when the concentration was increased activity of ion increased and this leads to increment on chemical potential. An increase in the chemical potential of ions leads to diffuse faster and more inside the sorbent, which causes an increase in capacity.

Obtained results are applied to isotherm models. Experimental isotherms are useful describing adsorption capacity to facilitate evaluation of the feasibility of this process for a given application, for selection of the most appropriate adsorbent, and for preliminary determination of adsorbent dosage requirements. For this purpose, Langmuir and Freundlich isotherm models are applied to experimental results.
The Langmuir isotherm equation presents a sorption model of a homogeneous system with a single layer, and its linear form is shown in Eqn. 9:

\[
\frac{C_e}{Q_e} = \frac{1}{bQ_0} + \frac{C_e}{Q_0} \quad \text{............. (9)}.
\]

Where \(Q_e\) (mg/g) is the amount of Cu\(^{2+}\) sorbed per gram of dry sorbent at equilibrium, \(C_e\) is the equilibrium concentration of Cu\(^{2+}\) in the solution (mg/L), \(Q_0\) (mg/g), and \(b\) (L/mg) are the Langmuir constants related to the capacity and energy of sorption, respectively.

The Freundlich model is known as the earliest empirical equation and is shown to be consistent with the exponential distribution of active centers, characteristic of heterogeneous surfaces. Freundlich equation is shown in Eqn. 10:

\[
\log Q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{......................... (10)}
\]

Where \(K_F\) and \(n\) are the Freundlich constants, which are indicative of relative capacity and adsorption intensity, respectively. The calculated isotherm parameters are shown in Table 5. The experimental data give better linearity with the Langmuir isotherm model compared to the Freundlich model. This result indicates that Cu\(^{2+}\) sorption on the composite sorbent can be depicted using Langmuir monolayer sorption. The maximum sorption capacity for Cu\(^{2+}\) ions on composites sorbent was found to be 4.2 mg/g. With regard to the Langmuir isotherm model, it is reported that the favorability of adsorption can be estimated using the separation factor or equilibrium parameter \(R_L\). Its value can be calculated using Eqn. 11:

\[
R_L = \frac{1}{1 + bC_0} \quad \text{................. (11)}
\]

where \(C_0\) (mg/L) is the initial solution concentration and \(b\) (L mg\(^{-1}\)) is the equilibrium constant of Langmuir adsorption. The parameter \(R_L\) indicate the shape of sorption isotherm and...
0 < \( R_L < 1 \) indicates the high-affinity sorption. In all worked concentration, \( R_L \) values were higher than 0 and lower than 1. Obtained results show that sorption of \( Cu^{2+} \) onto composite sorbent is favorable. The capacity of sorbent is compared with others reported in literature and results are summed up in Table 6.

\[ \text{<PLEASE INSERT TABLE 6 HERE>} \]

The capacity of prepared sorbent varies from 2.51 to 101.6 mg/g. The modification way and modification materials strongly affect sorption capacity. In this work, we used the co-precipitation method. During the preparation of sorbent, some active site of the cellulose (sulfonic acid groups) may be encapsulated in the magnetic particles, which are unavailable for \( Cu^{2+} \) sorption.

**Thermodynamic studies**

The thermodynamic parameters for the sorption process such as Gibbs free energy change (\( \Delta G^0 \)), enthalpy change (\( \Delta H^0 \)) and entropy change (\( \Delta S^0 \)) were calculated by using following equations:

\[ \Delta G^0 = -RT\ln K_e^0 \] ..........................(12)

\[ \ln K_e^0 = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \] ..........................(13)

\[ \Delta G^0 = \Delta H^0 - T\Delta S^0 \] ..........................(14)

In these equations, \( K_e \) is the equilibrium constant and it was calculated by \( q_e/C_e \). R is the universal gas constant (8.314 J/mol K), and T is the temperature (K). Parameters change in enthalpy (\( \Delta H^0 \)) and change in entropy (\( \Delta S^0 \)) are calculated from the slope and the intercept of the linear plot of \( \ln K_e \) vs. \( 1/T \) (Figure S3). The calculated thermodynamic parameters are
The positive value of the heat of sorption ($\Delta H^0$) suggests that the sorption of Cu$^{2+}$ onto sorbent is an endothermic process. The negative values of free energy change ($\Delta G^0$) indicate the spontaneous nature of the sorption process. The positive value of $\Delta S^0$ shows the increasing randomness at the solid/liquid interface during the sorption of copper ions on the prepared sorbent.

**Regeneration of sorbent**

Regeneration of the sorbent was carried out as explained in our previous work and obtained results were summarized in Table 8. It was found that the Cu$^{2+}$ ions could be effectively desorbed from composite sorbent using the 0.5 mol/L H$_2$SO$_4$ solution, with the desorption efficiency of over 99%.

**Conclusions**

In this study, sulfonated cellulose-magnetite composite sorbent was successfully prepared and characterized by IR, XPS, XRF, SEM, VSM and an elemental analyzer. The Cu$^{2+}$ ions can be effectively removed from aqueous solutions. Sorbent exhibited fast kinetic for Cu$^{2+}$ removal. The capacity of sorbent is highly pH depended and optimum removal achieved at pH $\geq$ 4. Removal of Cu$^{2+}$ follows pseudo-second-order kinetics. The maximum sorption capacity of sorbent found as 4.2 mg Cu$^{2+}$/g. The obtained thermodynamic variables demonstrated that sorption of Cu$^{2+}$ onto the composite sorbent was an endothermic and spontaneous process. In addition, the Cu$^{2+}$ ions could be effectively desorbed by a 0.5 mol/L H$_2$SO$_4$ solution.
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References

1. Z. F. Yang, L. Y. Li, C. Te Hsieh, and R. S. Juang, *J. Taiwan Inst. Chem. Eng.*, 2018, 82, 56.
2. H. Aydin, Y. Bulut, and Ç. Yerlikaya, *J. Environ. Manage.*, 2008, 87, 37.
3. Z. Aksu and I. A. Işoğlu, *Process Biochem.*, 2005, 40, 3031.
4. WHO, 2004, 03.4/88.
5. E. Parlak and Ö. Arar, *J. Dispers. Sci. Technol.*, 2018, 39, 1403.
6. D. Y. Zhang, N. Zhang, P. Song, J. Y. Hao, Y. Wan, X. H. Yao, T. Chen, and L. Li, *Carbohydr. Polym.*, 2018, 181, 560.
7. M. Zirak, A. Abdollahiyan, B. Eftekhar-Sis, and M. Saraei, *Cellulose*, 2018, 25, 503.
8. E. Özbunar, S. Kirca, Ö. Arar, and Ü. Yüksel, *Anal. Lett.*, 2017, 50, 1657.
9. O. Yayayürük, E. Henden, and N. Bicak, *Anal. Sci.*, 2011, 27, 833.
10. Q. Wu and Z. Xiong, *J. Disp. Sci. Technol.*, 2015, 36, 821.
11. X. Yu, S. Tong, M. Ge, J. Zuo, C. Cao, and W. Song, *J. Mater. Chem. A*, 2013, 1, 959.
12. M. Alfe, P. Ammendola, V. Gargiulo, F. Raganati, and R. Chirone, *Proc. Combust. Inst.*, 2015, 35, 2801.
13. T. Yamashita and P. Hayes, *Appl. Surf. Sci.*, 2008, 254, 2441.
14. A. C. Small and J. H. Johnston, *J. Colloid Interface Sci.*, 2009, 331, 122.
15. S. E.-S. Ghazy, S. E.-S. Samra, A. E.-F. M. Mahdy, and S. M. EL-Morsy, *Anal. Sci.*, 2006, 22, 377.
16. N. A. Fakhre and B. M. Ibrahim, *J. Hazard. Mater.*, 2018, 343, 324.
17. M. A. Güngör, Ö. Özlalp, and Ö. Arar, *Desal. Water Treat.*, 2017, 88, 279.
18. W. Rieman and H. F. Walton, "*Ion Exchange in Analytical Chemistry*" 1970. Pergamon press, Oxford.
19. G. McKay, Y. S. Ho, and J. C. Y. Ng, *Sep. Purif. Rev.*, 1999, 28, 87.
20. Y. S. Ho and G. McKay, *Process Biochem.*, **1999**, *34*, 451.

21. A. Z. M. Badruddoza, A. S. H. Tay, P. Y. Tan, K. Hidajat, and M. S. Uddin, *J. Hazard. Mater.*, **2011**, *185*, 1177.

22. X. Yi, J. He, Y. Guo, Z. Han, M. Yang, J. Jin, J. Gu, M. Ou, and X. Xu, *Ecotoxicol. Environ. Saf.*, **2018**, *147*, 699.

23. A. Asthana, R. Verma, A. K. Singh, and M. A. B. H. Susan, *J. Environ. Chem. Eng.*, **2016**, *4*, 1985.

24. A. Mittal, R. Ahmad, and I. Hasan, *Desalin. Water Treat.*, **2016**, *57*, 19820.

25. G. Neeraj, S. Krishnan, P. Senthil Kumar, K. R. Shriaishvarya, and V. Vinoth Kumar, *J. Mol. Liq.*, **2016**, *214*, 335.

26. M.J. Slater, “*Principles of Ion Exchange Technology*”, **1991**, First ed., Butterworth-Heinemann, London.

27. V. S. Bagotsky, “*Fundamentals of Electrochemistry: Second Ed.*”, **2005**, John Wiley & Sons, New Jersey.

28. F. L. Slejko, “*Adsorption Technology: A Step-By-Step Approach To Process Evaluation and Application.*”, **1985**, Marcel Dekker, New York.

29. B. Alyüz and S. Veli, *J. Hazard. Mater.*, **2009**, *167*, 482.

30. C. Marchioni, F. M. de Oliveira, C. S. de Magalhaes, and P. O. Luccas, *Anal. Sci.*, **2015**, *31*, 165.

31. N. M. El-Mallah and H. M. Hassouba, *J. Dispers. Sci. Technol.*, **2014**.

32. H. Hu, J. Zhang, K. Lu, and Y. Tian, *J. Environ. Chem. Eng.*, **2015**.

33. A. Mahapatra, B. G. Mishra, and G. Hota, *J. Hazard. Mater.*, **2013**.

34. M. Bystrzejewski, K. Pyrzyńska, A. Huczko, and H. Lange, Carbon-encapsulated magnetic nanoparticles as separable and mobile sorbents of heavy metal ions from aqueous solutions, **2009**.
35. A. M. Donia, A. A. Atia, and F. I. Abouzayed, *Chem. Eng. J.*, **2012**, *191*, 22.

36. Y.-T. Zhou, H.-L. Nie, C. Branford-White, Z.-Y. He, and L.-M. Zhu, *J. Colloid Interface Sci.*, **2009**, *330*, 29.

37. S. S. Banerjee and D. H. Chen, *J. Hazard. Mater.*, **2007**.

38. J. F. Liu, Z. S. Zhao, and G. Bin Jiang, *Environ. Sci. Technol.*, **2008**.

39. B. Aşçı, E. Kövenç, Ö. Arar, and M. Arda, *Glob. NEST J.*, **2018**, *20*, 368.

40. M. Duran, Ö. Arar, and M. Arda, *J. Chil. Chem. Soc.*, **2019**, *64*, 4399.

41. Ö. Arar, *Anadolu Univ. J. Sci. Technol. Appl. Sci. Eng.*, **2016**, *17*, 530.
List of Tables

Table 1: Experimental parameters for Cu$^{2+}$ removal

Table 2. Elemental analysis results of sorbent

Table 3: First-order and second-order rate constants for Cu$^{2+}$ sorption

Table 4: Comparison of pseudo-second-order rate constant for the sorption of Cu$^{2+}$ ions onto various sorbents.

Table 5: Isotherm model constants and correlation coefficients for the sorption of Cu$^{2+}$

Table 6: Comparison of sorption capacities of various sorbents

Table 7: Thermodynamic parameters for Cu$^{2+}$ removal by composite sorbent

Table 8: Desorption efficiency of regenerants.
Table 1 Experimental parameters for Cu$^{2+}$ removal

| Investigated parameter | Cu$^{2+}$ concentration/mg L$^{-1}$ | Sorbent dose /g | Volume of solution/mL | pH of solution | Temperature/°C |
|------------------------|------------------------------------|-----------------|------------------------|----------------|----------------|
| Sorbent dose           | 5.0 from 0.025 to 0.3              | 25              | 5                      | 25             |
| pH of solution         | 5.0 0.2                             | 25              | from 1 to 9            | 25             |
| Isotherm study         | from 50 to 500 0.2                 | 25              | 5                      | 25             |
| Temperature effect     | 5.0 0.2                             | 25              | 5                      | 40, 50 and 60  |
| Kinetic study          | 5.0 8.0                             | 1000            | 5                      | 25             |
Table 2 Elemental analysis results of sorbent

| Component     | Content, % |
|---------------|------------|
| Fe (as Fe₂O₃) | 54.74      |
| C             | 19.95      |
| H             | 3.480      |
| S             | 0.5100     |
Table 3 First-order and second-order rate constants for Cu$^{2+}$ sorption

| Kinetic model         | Parameter      | Calculated value |
|-----------------------|----------------|------------------|
|                       | $k_1 / \text{min}^{-1}$ | 0.128            |
| **Pseudo First order**| $q_e / \text{mg g}^{-1}$ | 0.0217           |
|                       | $R^2$          | 0.986            |
|                       | $k_2 / g \text{mg}^{-1} \text{min}^{-1}$ | 26.7             |
| **Pseudo Second order**| $q_e / \text{mg g}^{-1}$ | 0.587            |
|                       | $R^2$          | 0.999            |
Table 4 Comparison of pseudo-second-order rate constant for the sorption of Cu$^{2+}$ ions onto various sorbents.

| Sorbent                                                      | $k_2/\text{g mg}^{-1}\text{min}^{-1}$ | Equilibrium time/ minutes | references |
|-------------------------------------------------------------|---------------------------------------|---------------------------|------------|
| carboxymethyl--cyclodextrin modified Fe$_3$O$_4$ nanoparticles | 0.0380                                | 30                        | 21         |
| Humic acid coated magnetite                                  | $4.40 \times 10^{-4}$                | 180                       | 22         |
| Glycine functionalized magnetic nanoparticle                 | 2.85                                  | 160                       | 23         |
| entrapped calcium alginate beads                             |                                       |                           |            |
| Poly (methyl methacrylate)-grafted alginate/Fe$_3$O$_4$ nanocomposite | 0.0100                                | 180                       | 24         |
| Chitosan coated magnetic nanoparticles                       | 0.00240                               | 30                        | 25         |
| Sulfonated cellulose-magnetite                               | 26.7                                  | 15                        | This work  |
Table 5 Isotherm model constants and correlation coefficients for the sorption of Cu$^{2+}$

| Langmuir Isotherm Constants | Freundlich Isotherm Constants |
|-----------------------------|-----------------------------|
| $Q_{\text{max}}$/ mg g$^{-1}$ | $K_L/L$ mg$^{-1}$ | $R^2$ | $K_F$/mg g$^{-1}$ | $n$ | $R^2$ |
| 4.246 | 0.1180 | 0.9993 | 3.3280 | 27.83 | 0.8345 |
Table 6 Comparison of sorption capacities of various sorbents

| Sorbent                                      | $Q_0$/mg g$^{-1}$ | Reference |
|----------------------------------------------|-------------------|-----------|
| Acidosasa edulis shoot shell                 | 2.510             | 32        |
| Electrospun Fe$_2$O$_3$–Al$_2$O$_3$          | 4.980             | 33        |
| Carbon-encapsulated magnetic nanoparticles   | 3.210             | 34        |
| Nano-magnetic cellulose                     | 101.6             | 35        |
| Chitosan-coated magnetic nanoparticles      | 60.61             | 36        |
| gum arabic modified magnetic nano-adsorbent  | 38.50             | 37        |
| Humic Acid coated magnetite                 | 46.30             | 38        |
| Sulfonated cellulose-magnetite              | 4.246             | This work |

This work
Table 7 Thermodynamic parameters for Cu\(^{2+}\) removal by composite sorbent

| \(\Delta S / \text{J mol}^{-1} \text{ K}^{-1}\) | \(\Delta H / \text{kJ mol}^{-1}\) | \(\Delta G / \text{kJ mol}^{-1}\) |
|---|---|---|
| -15.8 (313 K) | 154 | 32.5 |
| -17.3 (323 K) | -18.8 (323 K) |
Table 8 Desorption efficiency of regenerants.

| Regenerated by | Regeneration, % |
|---------------|----------------|
| 0.1 M HNO₃    | 93             |
| 0.5 M HNO₃    | 96             |
| 0.1 M H₂SO₄   | 98             |
| 0.5 M H₂SO₄   | > 99           |
Figure Captions

Fig. 1 Magnetization curves of bare magnetite and hybrid sorbent.

Fig. 2 XPS spectrum of composite sorbent.

Fig. 3 Effect of sorbent dose on the removal of Cu$^{2+}$.

Fig. 4 Effect of initial solution pH on Cu$^{2+}$ removal.

Fig. 5 Removal of Cu$^{2+}$ versus time.

Fig. 6 Sorption isotherm of Cu$^{2+}$ ion.
Figure 1: Magnetization curves of bare magnetite and hybrid sorbent.
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Graphical Index

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[Chemical Structure Image]
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NaIO₄ → [Intermediate Structure] → Na₂S₂O₅ → [Final Structure]
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[Diagram showing Cu²⁺ sorption process]
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NaOH, Fe²⁺, Fe³⁺ → [Conjugated System]
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Cu²⁺ sorption
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