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Focusing on Eco-Friendly Adsorption Method: Removal of Endocrine-Disrupting Cu^{2+} Ions by Iron Shavings †

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Abstract: Today, the common problem of all countries of the world is the presence of different environmental pollutants in water, air and soil environments. In particular, endocrine disruptors represent a broad group of pollutants. Copper, which is both in this group and among the heavy metals, reaches aquatic environments directly and indirectly from anthropogenic activities. The adsorption process is the most environmentally friendly, economical and practical method to prevent pollution caused by these Cu^{2+} ions, and intensive studies have been carried out on this method in recent years. The main target in these studies is to prefer adsorbents that do not cause pollution after removal. In this study, iron shavings (FeS) was considered to be used as an adsorbent. Laboratory scale batch analyzes were performed in synthetic solution under constant stirring speed (150 rpm) and temperature (20 ± 2 °C) with different pH (2.0–6.0), FeS dose (0.1–5 g) and contact times (1–60 min). The maximum removal efficiency of Cu^{2+} was determined as 78% under optimum operating conditions. The aim of this research article is to understand the application possibility of FeS adsorbent for efficient removal of Cu^{2+}. Interestingly, laboratory studies have shown that the use of FeS adsorbent can efficiently remove the endocrine disrupting Cu^{2+}.

Keywords: adsorption; adsorbent; eco-friendly; copper ions; iron shavings

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1. Introduction

One of the high potential pollutant groups that endanger the health of humans and other living things is endocrine disrupting chemicals. Living habits, technological developments, production-oriented industrial activities increase their presence in the environment on an international scale. This group of pollutants is wide and they show disruptive effects on the hormonal system of living things. Heavy metals, dyes, pharmaceuticals and personal care products are at the forefront of endocrine disruptors [1,2]. Most heavy metals are toxic [3]. They are not biodegradable by natural mechanisms and accumulate in living things through the food chain [4]. According to the United States Environmental Protection Agency, seven heavy metals (Pb, Cr, Zn, Cu, Cd, Hg, Ni) are listed as the most common heavy metals in the environment [5,6]. Heavy metal pollution has been a research topic for many years. According to the Environmental Protection Agency, copper is the most common been trace metal in the environment. It has a structure that both supports the enzyme activities of living things and has a high poison level [7]. Copper is a widely used material in a wide variety of fields such as electronic appliances, construction, food preparation industry, energy industry, automobile industry, livestock, tanneries, cosmetics and jewelry. All these applications increase the use of copper and are reflected in the receiving waters as copper input [8,9]. High copper exposure can lead to anemia, gastrointestinal problems, hair loss and kidney failure [7,10]. As a result, wastewater containing copper ions (Cu^{2+}) must be treated before being discharged into the natural water flow. There are many methods for removing Cu2+ and other heavy metals from wastewater. These are listed as chemical precipitation, ion exchange, adsorption, electrocoagulation, membrane technologies [11]. Apart from adsorption, these methods have disadvantages such as expensive chemical requirements, low removal efficiencies and generation of secondary wastes. Among these methods, the adsorption process is more advantageous than other methods in terms of simple design, cheap, fast, and environmental friendliness [4,11]. In addition to adsorption, the adsorbent used should also be economical. Therefore, different alternatives have been evaluated [12,13]. Evaluation of some wastes originating from industrial sectors in this process is important in terms of both recovery and heavy metal removal. In particular, iron shavings (FeS) is produced in the iron and steel industry with high iron content and in areas where iron is used intensively [14]. The structural state of FeS facilitates its use as an adsorbent. FeS is evaluated in terms of different properties such as high selectivity, high adsorption capacity, active surface, pore distribution quality and surface functional groups. As a result, the treatment of Cu^{2+} ions of FeS as an adsorbent source under optimum adsorption conditions was evaluated. The primary aim of this study is to support a circular economy and to minimize the dangerous impact of waste. Therefore, the experimental results of this study can serve as a guide for the iron production industry in terms of waste management for the efficient and environmentally friendly treatment of wastewater containing metal ions. For this reason, the effects of optimum solution pH, contact time and amount of adsorbent on the adsorbent capacity were investigated and the results obtained were evaluated.

2. Materials and Method

All chemicals used in the experiments performed in batch mode were obtained from Merck Company. To prepare a 1000 mg/L copper stock solution, 3.928 g $CuSO_4.5H_2O$ was weighed and prepared with distilled water (Millipore Elix Advantage). In batch adsorption studies, solutions with a concentration of 100 mg/L prepared by diluting from the stock solution were used. Before adsorption, the initial pH values of the solutions were adjusted with a pH meter (HANNA pH 211). The waste raw material used in the research was collected from the relevant sector in the organized industrial site of Aksaray Province. The average size of non-uniform FeS is about 2 mm. FeS was washed with distilled water before being used as an adsorbent. It was then dried at room temperature. The surface morphology and element distribution of FeS were investigated by scanning electron microscopy (SEM/EDX) (Hitachi-SU 1510). The functional groups of the material were carried out with Perkin Elmer brand Fourier Transform Infrared Spectroscopy (FTIR) device in the range of 4000–500 cm^{-1}. Adsorption studies were carried out in a discontinuous order in 250 mL flasks with a closed mouth. In order to determine the amount of Cu^{2+} adsorbed, the filtered samples were analyzed in an inductively coupled plasma optical emission spectrometer (ICP-OES) (ICP-OES, 2100DV, Perkin Elmer, USA). After the adsorption reached equilibrium, the Cu^{2+} yield was calculated by the following formula.

$$Cu^{2+}(\%) = \frac{C_0 - C_e}{C_0} \times 100$$

3. Results and Discussion

3.1. FeS Morphological Element Analysis

The SEM and EDX distribution of FeS are shown in Figure 1. SEM images of the FeS surface before Cu^{2+} adsorption were examined at different magnifications and the results showed a heterogeneous, microporous surface (scaly and layered leaf appearance). The porous structure of FeS allows faster interaction with Cu^{2+} [7]. EDX analysis was used to determine the FeS surface composition (Figure 1). According to the elemental change analysis in FeS, by weight; It consists of the elements C (56.62%), O (7.51%), N (4.45%), F (4.37%), Fe (25.04%) and Si (2.02%). EDX spectra showed that FeS consisted mostly of C and Fe (Figure 1). This result can be referred to the fact that the adsorption mechanism of Cu^{2+} ions may be due to ion exchange [7,15].

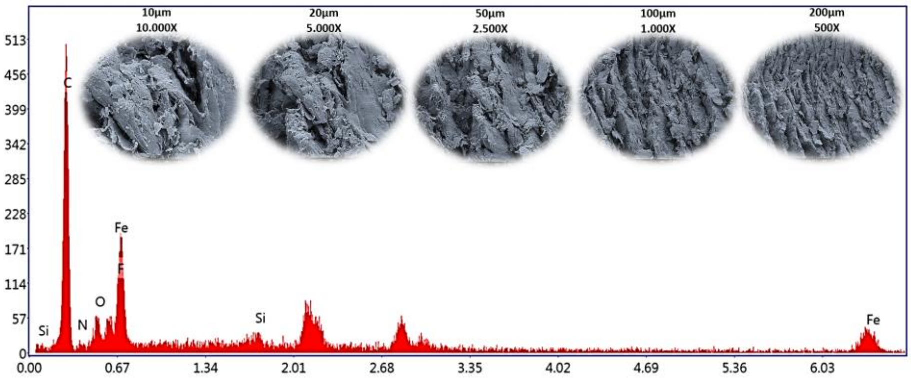

Figure 1. SEM images and EDX distribution of FeS.

In the FTIR analysis of adsorbent molecules, two regions are defined as the functional group region (4000–1500 cm^{-1}) and the fingerprint region (1500–500 cm^{-1}). The surface chemistry of FeS was performed by FTIR analysis (Figure 2). Eight different peaks (1405.63, 1393.75, 1249.80, 1065.97, 1056.89, 891.90, 668.12 and 581.25 cm^{-1}) were detected in the fingerprint region. In this region, special vibrations such as O-H, C=C and C-H bending and C-O, C-N, and S=O stretching take place. In the 4000–1500 cm^{-1} region, 3674.94, 2987.95, 2900.66 and 2359.53 cm^{-1} peaks are observed. These peaks form double (C=O, O=C=O) and single (O-H, N-H) bonds.

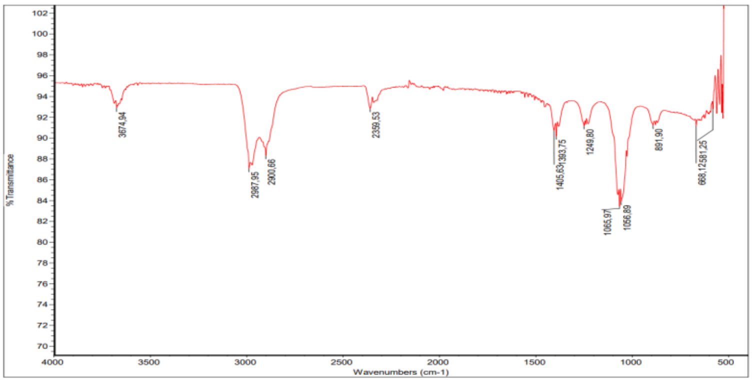

Figure 2. FTIR analysis image of FeS adsorbent.

3.2. *Effect of Adsorption Factors on Cu^{2+} Adsorption*

The adsorption efficiency changes due to the exchange of hydrogen (H^+), and hydroxyl (OH^-) ions of the aqueous solution. The pH of the environment is an important parameter that affects the interaction between both adsorbent and pollutant. Figure 3c shows the pH change of the study. As a result of the batch experiments carried out with 5 different pH values, the maximum Cu^{2+} removal efficiency of 79% was found at pH 4.00. At the acid level, chemical interaction is observed between the cations in solution and the main functional groups of FeS. In alkaline conditions, the adhesion of Cu^{2+} ions to the surface decreases. This may be due to the intense concentration of competitive hydroxyl anions. In addition, it is a known fact that the removal efficiency of the pollutant (Cu^{2+}) is shaped according to the loading of the adsorbent (FeS) surface.

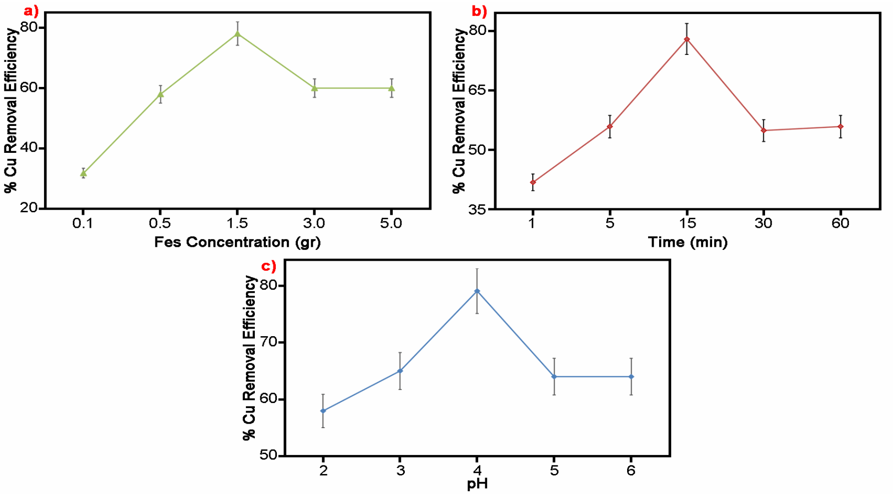

Figure 3. Changes of Cu^{2+} removal (**a**) FeS dose (*Time:15 min., pH: 4.0*), (**b**) Time (*FeS:1.5 g, pH: 4.0*), (**c**) pH (*Time:15 min., FeS: 1.5 g*).

The effect of FeS amount on Cu^{2+} removal was evaluated in the range of 0.1–5.0 g at 100 mg/L Cu^{2+} concentration at 20 ± 2 °C at 150 rpm. Cu^{2+} removal rate increased rapidly up to 1.5 g FeS dose and decreased at 3 and 5 g doses (Figure 3a). It can be said that this is due to the effective FeS surface area distribution. The maximum Cu^{2+} removal efficiency was found to be 78% at a dose of 1.5 g FeS. The decrease in yield after 1.5 g FeS dose may due to FeS saturation after sufficient Cu^{2+} has been adsorbed and therefore FeS cannot adsorb Cu^{2+} any more. As can be seen in Figure 3b, the contact time relationship between FeS and Cu^{2+} ions occurs in accordance with the adsorption process. The adsorption of Cu^{2+} on FeS was investigated as a function of time in the range of 1–60 min. Efficiency increased rapidly at the beginning, reaching a maximum of 78% within 15 min of contact time. The rapid adsorption process may be due to the denser free surface area of FeS for Cu^{2+} removal.

3.3. Isotherm and Kinetic Models Applied in Batch Experiments

Langmuir (L) and Freundlich (F) isotherms, which best describe the experimental data, were used to evaluate the maximum adsorption capacity. The most common models used to describe adsorption equilibria are Langmuir and Freundlich. The coefficients, correlation factors (R^2) and equations of the obtained isotherm parameters are listed in Table 1 [13]. Also, the essential properties of a Langmuir isotherm can be expressed by the dimensionless constant separation factor R_L. The R_L parameter shows the shape of the isotherm as follows: $R_L > 1$, unfavorable; $R_L = 1$, linear; $0 < R_L < 1$ is favorable and $R_L = 0$ is irreversible. The calculated maximum adsorption capacity was determined as 15.64 mg/g at q_m, 20 °C, with a contact time of 15 min and a Cu^{2+} concentration of 100 mg/L. Figure 4 shows the fit of the Langmuir and Freundlich isotherms to the experimental data. As can be seen in Table 1, the Langmuir model gave the best result to the experimental data of Cu^{2+} adsorption on FeS due to the highest correlation coefficient (0.999). The dimensionless fixed separation factor, R_L, was 0.3251 for an initial Cu^{2+} concentration of 282.1 mg/L, showing favorable adsorption for Langmuir in the range $0 < R_L < 1$. For Freundlich, the R^2 (0.6841) value remained low.

Table 1. Isotherm models, their linear forms and respective coefficient.

Models	Equations	Coefficients	
Langmuir	$q_e = \frac{q_m K_L C_e}{1 + K_L C_e}$ $R_L = \frac{1}{1 + K_L x C_e}$	q_m (mg/g)	15.64
		K_L (L/mg)	0.2978
		R_L	0.3251
		R^2	0.9987
Freundlich	$q_e = K_F \sqrt[n]{C_e}$	K_F (L/mg)	30.323
		n	1.8103
		R^2	0.6841
Pseudo First Order	$\mathrm{In}(q_e - q_t) = \mathrm{In} q_e - k_1 \times t$	k_1 (L/min)	0.0122
		q_e (mg/g)	9.36
		R^2	0.5950
Pseudo Second Order	$\frac{t}{q_t} = \frac{1}{k_2 \times q_e^2} + \frac{1}{q_w} t$	k_2 (g/mg/min)	0.1020
		q_e (mg/g)	15.45
		R^2	0.9903

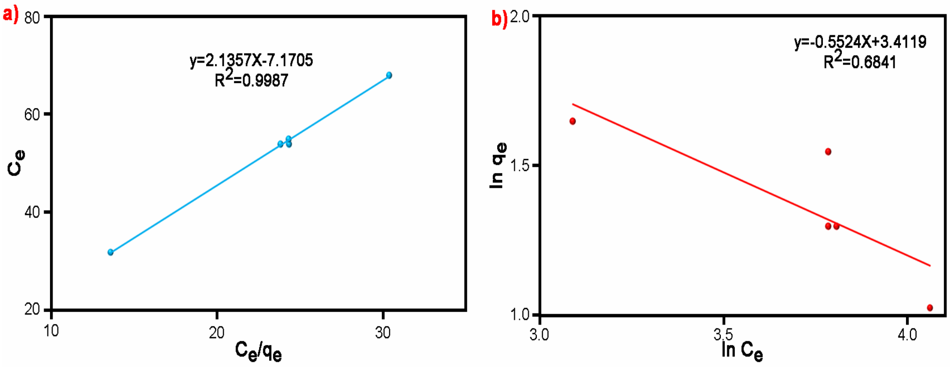

Figure 4. Variations of Cu^{2+} removal according to different adsorption parameters (**a**) Langmuir (**b**) Freundlich.

In this study, pseudo-first-order (PFO) and pseudo-second-order kinetic (PSO) models, which are widely used in the adsorption process, were tested (Figure 5). When the kinetic parameters were compared according to Table 1, the best correlation coefficient (R^2 = 0.9903) was found in the PSO model. Studies of Cu^{+2} ions with different adsorbents are also suitable for second-order kinetic modeling.

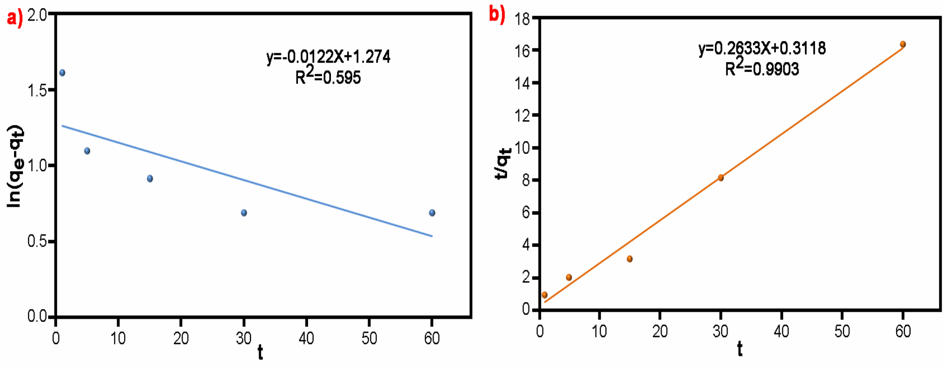

Figure 5. Kinetic curves of FeS and Cu^{2+} adsorption (**a**) PFO, (**b**) PSO.

4. Conclusions

The study data showed that the adsorption of Cu^{2+} on FeS surface was dependent on pH, contact time and FeS dose. The maximum Cu^{2+} removal rate of FeS was obtained as approximately 78% under optimum conditions (pH: 4.53, time: 15 min, FeS dose: 1.5 g).The system was found to be more suitable for Langmuir isotherm and pseudo-second order kinetics.

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References

1. Puri, M.; Gandhi, K.; Kumar, M.S. A global overview of endocrine disrupting chemicals in the environment: Occurrence, effects, and treatment methods. *Int. J. Environ. Sci. Technol.* 2023, *in press*. https://doi.org/10.1007/s13762-022-04636-4.
2. Dong, M.; He, L.; Jiang, M.; Zhu, Y.; Wang, J.; Gustave, W.; Wang, S.; Deng, Y.; Zhang, X.; Wang, Z. Biochar for the Removal of Emerging Pollutants from Aquatic Systems: A Review. *Int. J. Environ. Res. Public Health* **2023**, *20*, 1679. https://doi.org/10.3390/ijerph20031679.
3. Al Anazi, M.; Abdulazeez, I.; Al Hamouz, O.C.S. Selective Removal of Iron, Lead, and Copper Metal Ions from Industrial Wastewater by a Novel Cross-Linked Carbazole-Piperazine Copolymer. *Polymers* **2022**, *14*, 2486. https://doi.org/10.3390/polym14122486.
4. Darweesh, M.A.; Elgendy, M.Y.; Ayad, M.I.; Ahmed, A.M.; Elsayed, N.; Hammad, W. Adsorption isotherm, kinetic, and optimization studies for copper (II) removal from aqueous solutions by banana leaves and derived activated carbon. *S. Afr. J. Chem. Eng.* **2022**, *40*, 10–20. https://doi.org/10.1016/j.sajce.2022.01.002.
5. Gharbia, A.S.; Zákányi, B.; Tóth, M. Experimental and numerical study for the adsorption behavior of Cu(II) and Mn(II) in quartz sand. *Sustain. Water Resour. Manag.* **2022**, *8*, 126. https://doi.org/10.1007/s40899-022-00725-x.
6. Boluspayeva, L.; Jakubus, M.; Spychalski, W.; Abzhalelov, A.; Bitmanov, Y. Health Risk of Heavy Metals Related to Consumption of Vegetables in Areas of Industrial Impact in the Republic of Kazakhstan—Case Study for Oskemen. *Int. J. Environ. Res. Public Health* **2022**, *20*, 275. https://doi.org/10.3390/ijerph20010275.
7. Fawzy, M.A.; Al-Yasi, H.M.; Galal, T.M.; Hamza, R.Z.; Abdelkader, T.G.; Ali, E.F.; Hassan, S.H.A. Statistical optimization, kinetic, equilibrium isotherm and thermodynamic studies of copper biosorption onto Rosa damascena leaves as a low-cost biosorbent. *Sci. Rep.* **2022**, *12*, 8583. https://doi.org/10.1038/s41598-022-12233-1.
8. Zeng, G.; He, Y.; Liang, D.; Wang, F.; Luo, Y.; Yang, H.; Wang, Q.; Wang, J.; Gao, P.; Wen, X.; et al. Adsorption of Heavy Metal Ions Copper, Cadmium and Nickel by Microcystis Aeruginosa. *Int. J. Environ. Res. Public Health* **2022**, *19*, 13867.
9. Liao, W.; Zhu, Z.; Feng, C.; Yan, Z.; Hong, Y.; Liu, D.; Jin, X. Toxicity mechanisms and bioavailability of copper to fish based on an adverse outcome pathway analysis. *J. Environ. Sci.* **2023**, *127*, 495–507. https://doi.org/10.1016/j.jes.2022.06.002.
10. Çelebi, H. Use of Bioballs as an Adsorbent for the Removal of Copper. *J. Chem. Soc. Pak.* **2021**, *43*, 114–123.
11. Mongioví, C.; Crini, G. Copper Recovery from Aqueous Solutions by Hemp Shives: Adsorption Studies and Modeling. *Processes* **2023**, *11*, 191. https://doi.org/10.3390/pr11010191.
12. Chou, M.-Y.; Lee, T.-A.; Lin, Y.-S.; Hsu, S.-Y.; Wang, M.-F.; Li, P.-H.; Huang, P.-H.; Lu, W.-C.; Ho, J.-H. On the removal efficiency of copper ions in wastewater using calcined waste eggshells as natural adsorbents. *Sci. Rep.* **2023**, *13*, 1–13. https://doi.org/10.1038/s41598-023-27682-5.
13. Celebi, H.; Bilican, I.; Bahadir, T. Applicability of innovative adsorbents in geogenic arsenic removal. *J. Clean. Prod.* **2021**, *327*, 129475. https://doi.org/10.1016/j.jclepro.2021.129475.
14. Matei, E.; Predescu, A.M.; Șăulean, A.A.; Râpă, M.; Sohaciu, M.G.; Coman, G.; Berbecaru, A.-C.; Predescu, C.; Vâju, D.; Vlad, G. Ferrous Industrial Wastes—Valuable Resources for Water and Wastewater Decontamination. *Int. J. Environ. Res. Public Health* **2022**, *19*, 13951. https://doi.org/10.3390/ijerph192113951.
15. Wołowicz, A.; Staszak, K.; Hubicki, Z. Removal of Copper(II) in the Presence of Sodium Dodecylobenzene Sulfonate from Acidic Effluents Using Adsorption on Ion Exchangers and Micellar-Enhanced Ultrafiltration Methods. *Molecules* **2022**, *27*, 2430. https://doi.org/10.3390/molecules27082430.