J. Serb. Chem. Soc. 91 (0) 1–14 (2026) *Original scientific paper*
JSCS–13520 Published dd mm 2026

Silica modified with choline chloride/urea DES for ligand-free Cu(II) adsorption

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(Received 29 August, revised 20 November 2025, accepted 20 February 2026)

Abstract: In this study, silica modified with a hydrophilic deep eutectic solvent (DES) composed of choline chloride and urea (DES-Si) was synthesized and evaluated for ligand-free Cu(II) removal from aqueous solutions. The DES-Si was successfully characterized using Fourier transform infrared spectroscopy, thermogravimetric analysis, nuclear magnetic resonance and elemental analysis, confirming the effective immobilization of DES onto the silica surface. Batch adsorption experiments demonstrated that DES-Si achieved a Cu(II) removal efficiency exceeding 95 % under optimal conditions (pH 8, initial Cu(II) concentration 5 mg L^{-1}, contact time 45 min, at 25 °C). The maximum adsorption capacity obtained from the Langmuir model was 17.54 mg g^{-1}, indicating strong affinity toward Cu(II) ions. Kinetic studies revealed that the adsorption process followed the pseudo-second-order model (R^2 = 0.9964), suggesting that the rate-limiting step is governed by surface interactions. Equilibrium data were well described by the Langmuir, Freundlich and Temkin isotherm models, with the Temkin model providing the best fit (R^2 = 0.9914). Comparative studies showed that Cu(II) removal using DES-Si without a chelating ligand was significantly more efficient than in the presence of 1,10-phenanthroline, highlighting the effectiveness of ligand-free adsorption. These findings demonstrate that DES-Si is a promising and environmentally friendly adsorbent for efficient Cu(II) removal from aqueous media.

Keywords: deep eutectic solvent; silica modification; copper adsorption; ligand-free removal.

INTRODUCTION

Copper is a metal known for its excellent thermal and electrical conductivity, ease of fabrication, and good corrosion resistance. As a result, it is widely used in

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https://doi.org/10.2298/JSC250829011A

industries such as electroplating, mining and smelting, brass manufacturing and petroleum refining. Cu(II) is also essential for living organisms in ultra-trace amounts, playing key roles in antioxidant defense, cellular iron metabolism and cellular respiration.[1] However, excessive levels of Cu(II) are potentially toxic to aquatic life, humans and the environment.[2] Therefore, the removal of Cu(II) from industrial effluents is critical to protect water resources.[2] Adsorption technology is one of the most promising methods for Cu(II) removal.[3] Various materials, including activated carbon, natural bentonite, montmorillonite and rice husk, have been employed for this purpose.[4–7] However, many of these adsorbents suffer from limitations such as long equilibrium times, low removal capacities and selectivity and poor thermal stability.[7] To overcome these drawbacks, silica-based adsorbents have been explored due to their large specific surface area, uniform pore structure, and easily modifiable surface properties.[9] Organically modified silicas, in particular, have attracted considerable attention as promising adsorbents capable of enhancing the removal efficiency of heavy metals.[10]

Deep eutectic solvents (DESs) are a class of environmentally friendly solvents created by combining quaternary ammonium salts with hydrogen bond donors. These unique mixtures possess several beneficial characteristics, such as minimal vapor pressure, low toxicity, affordability and excellent biodegradability.[11] Due to these advantages, DESs have gained increasing recognition and are now employed in a wide range of scientific and industrial areas, including organic synthesis, electrochemical applications, materials engineering, biological studies, separation processes and chemical analysis.[12] A pioneering example of their use was demonstrated by Abbott *et al.*, who applied a DES made from chlorocholine chloride and urea (ChCl–urea) to modify cellulose structures.[12]

Recently, ionic liquids (ILs)-modified silica were successfully applied as stationary phases in liquid chromatography and as adsorbents.[13] However, it is challenging to prepare large-scale ILs in industry, because of complicated synthetic processes and the expensive raw material chemicals.[14] Hence, the low cost of deep eutectic solvents (DESs), which are ionic liquids analogues, was introduced.[15] DESs are formed by mixing a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) at a certain ratio and temperature.[15] DES appear to have useful properties, such as being easily prepared with high purity, nontoxic, inert in water and biodegradable.[15] The properties of DESs can be customized to a particular type of chemistry.[15] Owing to these attractive characteristics, attention had been given to DES as an alternative, environmentally friendly solvent and media for organic and inorganic reactions and separations.[16]

In recent years, DES-based mesoporous silica has been explored as an alternative stationary phase and adsorbent for size-exclusion chromatography columns.[17] However, their application as adsorbents for heavy metal removal, parti-

cularly Cu(II), remains underexplored. In this study, the feasibility of DES-modified silica (DES-Si) for Cu(II) removal from aqueous solutions was investigated. The DES was composed of choline chloride (HBA) and urea (HBD) and was immobilized onto silica to form DES-Si. This material was then used for Cu(II) adsorption without the addition of a chelating agent.[18] Although ligands such as 1,10-phenanthroline (phen) are commonly used for trace metal separation due to their specificity and selectivity, despite their toxicity character is far from environmentally friendly criteria.[18] As a comparison, the removal of Cu(II) was constructed using DES-Si with the presence of 1,10-phenanthroline (phen) in aqueous solution. The optimum conditions, such as pH, contact time and initial concentration of Cu(II), had been investigated to obtain efficient removal. In addition, the kinetic and isotherm studies were also conducted to identify the mechanism of adsorption.

EXPERIMENTAL

Chemicals

All reagents and chemicals used for the synthesis of DES-Si were analytical grade and used without further purification. Urea was purchased from Fluka-BioChemika (≥ 99.5 %). Choline chloride (ChCl) was acquired from Sigma-Aldrich (≥ 98 %). 1,10-Phenanthroline monohydrate (phen) was obtained from Systerm Chemicals (Shah Alam, Selangor, Malaysia). Ultrapure water type I was filtered from an ultrapure water system (Division of Millipore, USA).

Instrumentations

The Fourier transform infrared spectroscopy (FT-IR) was obtained from the Systerm 2000 PerkinElmer set, with the wavenumber between 400 and 4000 cm^{-1} at a scan rate of 8 scans per min. The thermogravimetric analysis (TGA) was collected from PerkinElmer STA 6000. The nuclear magnetic resonance (NMR) spectrum was analyzed using a Bruker Avance III 500 MHz. The carbon, hydrogen and nitrogen contents of silica, DES and DES-Si were determined by elemental analysis using PerkinElmer CHN elemental analyzer 2400 Series II. Atomic absorption spectrometer (AAS) analysis was obtained from a fully computer-controlled PerkinElmer absorption spectrometer Analyst 400.

Preparation and characterization of DES and DES-Si

The DES was prepared as previously reported by mixing choline chloride (ChCl) and urea in a 1:2 mole ratio, followed by constant heating and stirring at 80 °C for 2 h until a clear homogeneous liquid was obtained.[19] Silica has been activated to react with DES. The synthesis schemes for DES and DES-Si are shown in Fig. 1a and b, respectively. The crude product of DES-Si was obtained by heating at 80 °C for 15 h. Then, the DES-Si was filtered, washed with ultrapure water to remove impurities and unreacted DES, and dried at 100 °C for 6 h. Both DES and DES-Si were characterized using FT-IR, TGA, NMR and elemental analysis.

Preparation of standard and working solutions

100 mg L^{-1} Cu(II) solution was prepared freshly from 1000 mg L^{-1} of Cu(II) standard solution. A series of standard solutions for calibration analysis was prepared with concentrations of 1, 2, 3, 4 and 5 mg L^{-1} diluted with ultrapure water from a 100 mg L^{-1} solution. 100 mg L^{-1} of Cu(II) working solution was prepared in 100 mL volumetric flask by dissolving $CuSO_4 \cdot 5H_2O$ with ultrapure water.

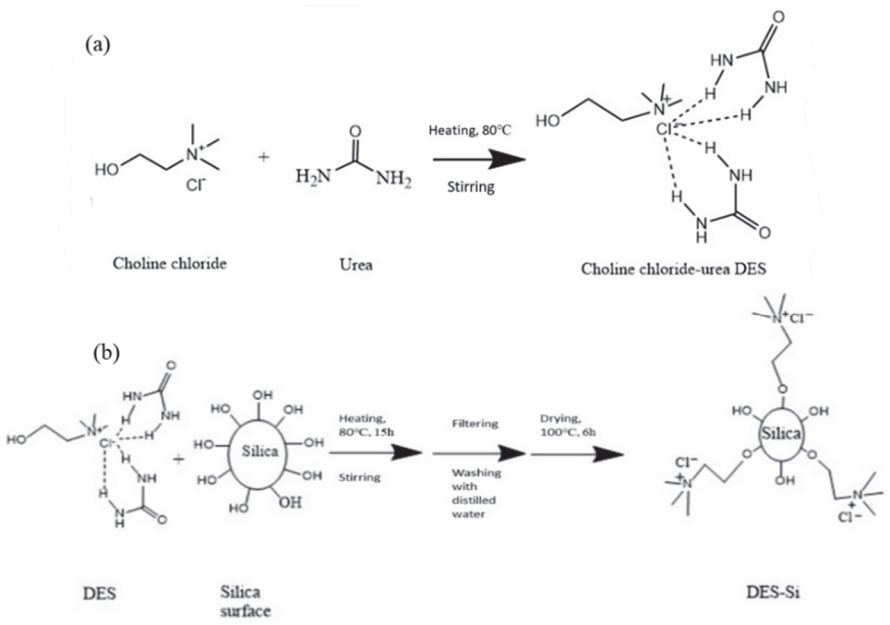

Fig. 1 Synthesis scheme of: a) DES and b) DES-Si.

Optimization parameters for the removal of Cu(II) ions

Effect of pH. A series of Cu(II) working solutions (20 mg L^{-1}) was adjusted to the desired pH range (2–8) using 0.1 M NaOH and 0.1 M HCl at 25 °C. For each pH, 20 mL of solution was mixed with 0.05 g of DES-Si and vortexed to ensure uniform dispersion. The mixture was allowed to equilibrate for 30 min (contact time) to enable Cu(II) adsorption. Afterward, the mixture was centrifuged to separate the solid adsorbent from the solution. The supernatant was filtered and analyzed using AAS. For comparison, 0.01 M phen was added to the Cu(II) solutions of varying pH, and the same procedure was followed.

Effect of contact time. A series of working solutions (20 mg L^{-1}) with optimum pH were mixed with 0.05 g DES-Si and allowed to contact at various time intervals (5, 10, 20, 30, 40 and 45 min) at 25 °C using a vortex and a centrifuge. The solutions were filtered and analyzed using AAS. Meanwhile, 0.01 M phen was added to each Cu(II) solution at the optimum pH, and the solutions were centrifuged for various times.

Effect of initial concentration. The initial concentrations of Cu(II) solutions were prepared as follows: 5, 10, 15, 20, 25 and 30 mg L^{-1}. Each solution was adjusted to the optimum pH, mixed with 0.05 g DES-Si and allowed to contact for the optimum time using a vortex and a centrifuge. The solutions were filtered and analyzed using AAS. Meanwhile, 0.01 M of phen was added to Cu(II) solutions with various concentrations and proceeded with the same procedure as above.

RESULTS AND DISCUSSION

Characterization

FT-IR. The FT-IR spectra exhibit various absorption bands, indicating different functional groups in DES and DES-Si. The functional groups and their

corresponding wave numbers (cm^{-1}) are listed in Table I. Fig. 2 shows the FT-IR spectra of ChCl, urea, activated silica, DES and DES-Si. The appearance of bands associated with ChCl, such as ν_{as}(OH), δ_{as}(OH), $\rho(CH_3)$, $\rho(CH_2)$, ν(C–O), ν_{as}(CCO) and $\nu_s(N–CH_3)$ in the spectrum of DES confirms that no destruction of Ch^+ structure occurs.[20] The absorption peaks of urea at 3430 and 3332 cm^{-1} were shifted towards the lower regions (3317 and 3190 cm^{-1}) and gained broader peaks due to the formation of additional hydrogen bonds, such as OH–O, OH–N and OH–OH, between ChCl and urea.[20] From Fig. 2, the spectrum for DES-Si shows a broad peak for ν_{as}(OH), δ_{as} of NH_2, Si–O–C and Si–O–Si strong absorption bands, ν_{as}(CCO) and $\nu_s(N–CH_3)$ at 3460, 1639, 1103, 970 and 802 cm^{-1}, respectively. The presence of these peaks confirms the attachment of DES to the activated silica.[19] The spectrum for activated silica shows the existence of bands associated with Si–O–Si and OH at 1099 and 3441 cm^{-1}, respectively. These bands indicate the presence of an active site on activated silica, where the modification process can occur.[21]

TABLE I. Wave numbers (cm^{-1}) and their assignment for FT-IR spectra; ν = stretching; δ = bending; ρ = rocking; ω = weak

Assignments	Adsorbent	
	DES	DES-Si
ν_{as}(OH)	3317	3460
$\nu_s(NH_2)$	3190	–
$\delta_s(NH_2)$	1663	–
ν(C=O)	1608	
δ_{as}(OH)	3025	–
$\delta_{as}(NH_2)$	–	1639
$\rho(CH_3)$	1476	–
$\rho_s(NH_2)$	1433	–
ν_{as}(CN)	1169	–
ν_{as}(Si–O–Si)	–	1103
ν_{as}(Si–O–C)		
$\rho(CH_2)$	1082	–
ν(C–O)	1005	–
ν_{as}(CCO	952	970
$\nu_s(N–CH_3)$	865	–
ω(C=O)	783	–
$\nu_s(N–CH_3)$	–	802
δ(N–H)	692	–

TGA. TGA analysis was performed to investigate the decomposition patterns of DES and DES-Si. The TGA analysis for all compounds is shown in Fig. 3. For the DES sample, TGA shows the first composition at 61 °C due to the loss of water. Meanwhile, there were compositions of ChCl and urea at 220 and 306 °C, respectively.[22] After immobilization onto the silica, the weight of DES-Si did not change

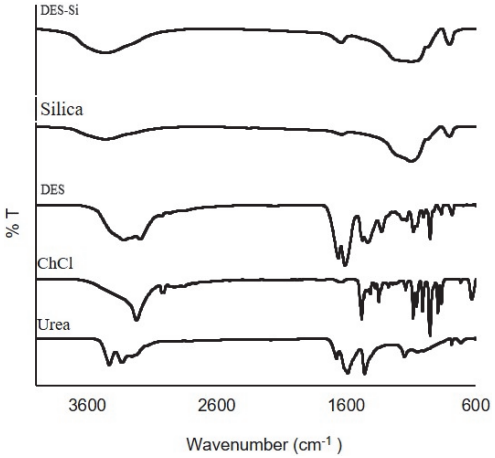

Fig. 2. FT-IR spectra for urea, ChCl, DES, activated silica and DES-Si.

significantly, thus making it stable at high temperatures. The total weight loss of DES-Si upon heating from 250 to 700 °C was less than 2 %, due to the desorption of water and the degradation of organic components before TGA.[19] Therefore, only a small amount of fly ash was released from the compounds in the TGA analysis.

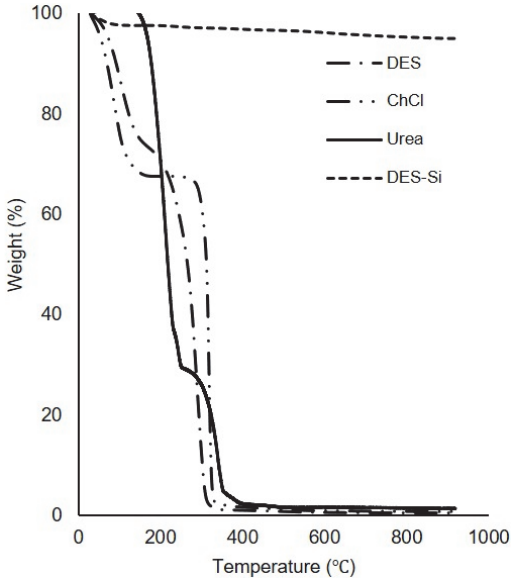

Fig. 3. TGA analysis of urea, ChCl, DES, and DES-Si.

NMR. The structure and spectra of DES, urea, and ChCl were deduced from ^{1}H-NMR (refer to Fig. S-1a–c of the Supplementary material to this paper) with tabulated assignment of functional groups in Table II. The spectrum of DES (Fig. S-1a) consisted of multiplet peaks for the NH_2 (δ5.76 ppm, 8H) and a singlet peak

for the deuterium hydroxide oxide (HDO) (δ 3.70 ppm, 1H),[23] attributed to the urea. The presence of HDO is due to the trace of water detected in DES given by its hygroscopic nature.[23] The spectrum of DES also shows the peaks of choline chloride through the existence of a singlet peak for the OH (δ 5.60 ppm, 1H), multiplet peaks for CH_2 (δ3.80 ppm, 2H; δ3.43 ppm, 2H), and multiplet peaks for $(CH_3)_3$ (δ3.14 ppm, 9H).

TABLE II. ^{1}H-NMR analysis of urea, ChCl and DES

Sample	Assignment	δ / ppm
Urea	HDO	3.38
	$R(–NH_2)_2$	5.45
ChCl	OH	5.70
	$CH_2(2)$	3.81
	$CH_2(1)$	3.45
	$N(CH_3)_3$	3.16
DES	$R(–NH_2)_2$	5.76
	OH	5.60
	HDO	3.70
	$CH_2(2)$	3.80
	$CH_2(1)$	3.43
	$N(CH_3)_3$	3.14

CHN analysis. From Table III, the distribution of the elements detected was 1.32 (C), 0.97 (H) and 0.54 % (N) in DES-Si, 0.14 (C), 0.76 (H) and 0.08 % (N) for activated silica and 28.2 (C), 8.81 (H) and 22. 92 % (N) in DES. The presence of nitrogen in DES-Si confirms that the DES was successfully immobilized onto silica. The detection of small amounts of nitrogen and carbon in silica may be due to contamination during sample preparation, which led to the adsorption of impurities onto the silica surface. Although DES-Si shows a significant increase in elemental content compared to unmodified silica, its C, H and N percentages are substantially lower than those of pure DES. This is expected, as only a thin layer of DES is coated onto the silica surface during immobilization, rather than forming a bulk DES material. Therefore, the comparatively lower elemental percentages in DES--Si reflect this partial surface coverage. Such a thin coating not only confirms efficient immobilization but also helps preserve the silica support's porosity and structural integrity.

TABLE III. Elemental analysis of DES-Si, silica and DES

Sample	Element content, %		
	C	H	N
DES-Si	1.32	0.97	0.54
Silica	0.14	0.76	0.08
DES	28.2	8.81	22.92

196 *Optimization parameters for the removal of Cu(II)*

197 The percentage removal of Cu(II) was calculated as:

198 $$\text{Removal} = 100\frac{c_0 - c_e}{c_0} \quad (1)$$

199 where c_0 is the initial adsorbate concentration (mg L^{-1}) and c_e is the equilibrium
200 concentration of the adsorbate (mg L^{-1}).

201 *Effect of pH*. The pH of the metal solution plays a crucial role in adsorption
202 studies. In this experiment, the removal of Cu(II) using DES-Si and DES-Si–phen
203 was carried out over a pH range of 1 to 8. The removal of Cu(II) (Fig. 4), with and
204 without ligand, was found to increase as the pH of the solution increased from 4 to
205 8. This result indicates that Cu(II) removal using DES-Si is favored under alkaline
206 conditions. At lower pH, the concentration of H_3O^+ greatly exceeds that of Cu(II),
207 leading to competitive binding at the active sites on DES-Si. At higher pH, the
208 concentration of H_3O^+ is lower, allowing a greater number of Cu(II) ions to bind
209 to the surface. The adsorption mechanism primarily involves electrostatic interact-
210 ions and surface complexation between divalent Cu^{2+} and negatively charged
211 functional groups present on the DES-modified silica surface. These interactions
212 are more favorable at higher pH values, where proton competition is reduced. The
213 H_3O^+ is replaced by metal ion and metal species such as Cu^{2+}, $CuOH^+$ and
214 $Cu_2(OH)_2^{2+}$. However, an increase in pH may also promote the precipitation of
215 Cu(II) as metal hydroxides. In this study, the pH was adjusted to 8 and precipitation
216 was monitored throughout to ensure none occurred. The solution at pH 8 was
217 confirmed to be free from precipitation. Based on Fig. 4, the removal efficiency of
218 Cu(II) using DES-Si reached 83.67 %, compared to 55.52 % for DES-Si–phen at
219 the same pH. Therefore, the optimal pH for Cu(II) adsorption in this system is pH 8.

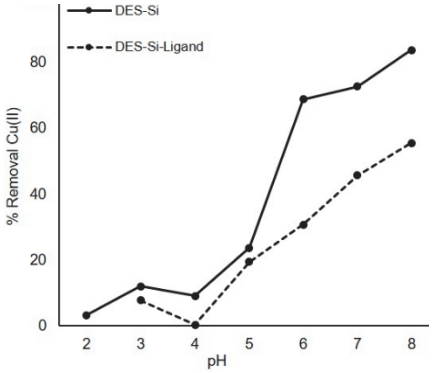

Fig. 4. Effect of pH on adsorption of Cu(II) (conditions: sorbent: 50 mg; initial concentration: 30 mg L^{-1}; volume: 20 mL; contact time: 30 min; temperature: 25 °C).

220 *Effect of contact time*. Contact times ranging from 5 to 45 min were inves-
221 tigated for the removal of Cu(II) using DES-Si and DES-Si–phen. The result in
222 Fig. 5 shows that the removal percentage increases with increasing contact time

for DES-Si and DES-Si–phen. The percentage removal of Cu(II) was slightly constant from 5 min and increased to 90.29 % for DES-Si and 53.15 % for DES--Si–phen at 45 min contact time. Overall, the result shows that the percentage removal of Cu(II) aqueous assisted phen is lower than the removal of Cu(II) without ligand. The lower removal of Cu(II) when phen is present can be explained by how it interacts with the Cu(II) ion. Phen forms strong, stable complexes with Cu(II) in the solution. Because of this, fewer free Cu(II) ions are available to bind to the DES-Si surface. These Cu–phen complexes might also have different charges or shapes, making them less likely to interact with the functional groups on DES-Si. As a result, the presence of phenanthroline interferes with the adsorption process rather than aiding it. The optimum contact time of 45 min was used for the next optimization for the removal of Cu(II).

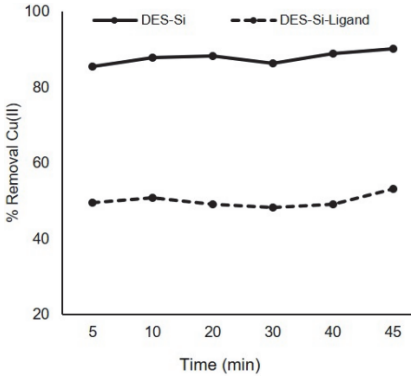

Fig. 5. Effect of contact time on adsorption of Cu(II) (conditions: pH: 8; sorbent: 50 mg; initial concentration: 30 mg L^{-1}; volume: 20 mL; temperature: 25 °C).

Effect initial concentration of Cu(II). The effect of the initial Cu(II) ion concentration on the adsorption performance of DES-Si and DES-Si–ligand was systematically investigated over a concentration range of 5–30 mg L^{-1} to evaluate their removal behavior. As illustrated in Fig. 6, DES-Si exhibited consistently high

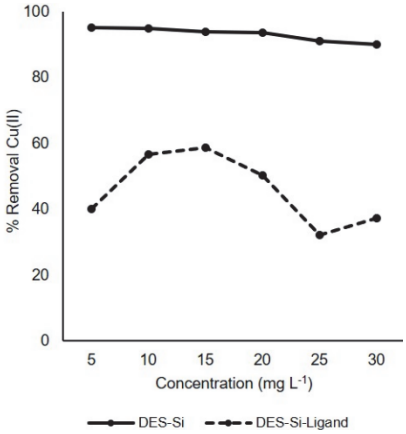

Fig. 6. Effect of initial concentration of Cu (II) (conditions: pH: 8; sorbent: 50 mg; contact time: 45 min; volume: 20 mL; temperature: 25 °C).

Cu(II) removal efficiency across the studied concentration range, with only a slight decrease at higher concentrations. This observation indicates the presence of sufficient active adsorption sites and a strong affinity between Cu(II) ions and the DES-Si surface. In contrast, the removal efficiency of DES-Si–ligand increased with increasing initial Cu(II) concentration up to 15 mg L^{-1}, after which a noticeable decline was observed at higher concentrations. This trend can be attributed to the saturation of available adsorption sites and increased competition among Cu(II) ions at elevated concentrations. Overall, DES-Si demonstrated superior adsorption performance compared to DES-Si–ligand throughout the investigated concentration range, highlighting its enhanced effectiveness for Cu(II) removal.

Batch adsorption studies

Adsorption kinetics. Adsorption kinetics is defined as the residence time of the sorbate onto the interface of the solid sorbent, controlled by the removal rate of the solute. The purpose of this study is to investigate the adsorption mechanism and the rate-controlling steps. Pseudo-first and second-order kinetic equations (Supplementary material) were applied to describe the adsorption of the adsorbate in an aqueous system onto the solid surface of the adsorbent.[8,26]

Δq (%) and *RE* (%) are the normalized standard deviation value and relative error, respectively, which were calculated to determine the stability and the fitness of the model to describe the kinetics of adsorption. The smaller the value of Δq and *RE*, the better the model fits.

By comparing the correlation coefficient (R^2) values of PFO and PSO (Table IV), it can be concluded that both sets of experimental data follow the PSO involving a chemisorption mechanism. In this mechanism, adsorption is driven by a chemical reaction at the exposed surface.[24,25]

TABLE IV. Details of the parameters and correlation coefficient of adsorption kinetic models

Kinetic model	Parameter	Removal Cu (II)	
		DES-Si	DES-Si–ligand
Pseudo first order	$q_{e,exp}$ / mg g^{-1}	6.604	3.776
	$q_{e,calc}$ / mg g^{-1}	0.6714	0.2667
	k_1	0.04813	–0.01888
	R^2	0.2343	0.4577
	Δq / %	40.17	41.56
	RE / %	89.83	92.94
Pseudo second order	$q_{e,calc}$ / mg g^{-1}	6.333	3.560
	k_2 / g mg^{-1} min^{-1}	–2.899	0.3933
	h / mg g^{-1} min^{-1}	–116.3	4.985
	$t_{1/2}$ / min	–0.4578	0.1105
	R^2	0.9964	0.9873
	Δq / %	1.84	2.56
	RE / %	4.10	5.72

Adsorption isotherm. An adsorption isotherm is a model that explains the affinity for the adsorbent and the surface properties. The result obtained can be used to explain the interaction that occurred between the adsorbate and the adsorbent. The adsorption mechanism of Cu(II) on DES-Si was studied using adsorption models, namely Langmuir, Freundlich, Temkin and Dubinin–Redushkevich.[8,26,27] The details ar given in the Supplementary material. The parameters obtained from the isotherm models were represented in Table V.

TABLE V. Details of parameters and correlation coefficient of adsorption isotherm models for adsorption of Cu (II) ion onto DES-Si

Isotherm model	Parameter	Value
Langmuir	q_m / mg g^{-1}	17.54
	b / L mg^{-1}	0.5231
	R_L	0.09911
	R^2	0.9887
Freundlich	n	1.4395
	K_F / mg g^{-1}	5.5424
	R^2	0.976
Temkin	b_T / J mol^{-1}	711.17
	S_T / L g^{-1}	6.4887
	R^2	0.9914
Dubinin–Radushkevich	q_m / mg g^{-1}	9.5172
	β / mol^2 kJ^{-2}	0.1031
	E / kJ mol^{-1}	2.2022
	R^2	0.9663

Based on the results obtained in Table V, it can be found that the value of R^2 is 0.9663, suggesting that these experimental data did not fit the Dubinin–Radushkevich isotherm model, indicating that the adsorption process does not follow this model. Result showed the mean free energy, E, of 2.2022 kJ mol^{-1} indicates that adsorption Cu(II) ions onto DES-Si is mainly physisorption because when a mean free energy is less than 8 kJ mol^{-1}, physisorption controls the adsorption mechanism, while chemisorption prevails when the mean free energy is in the range of 8 and 16 kJ mol^{-1}.[24]

CONCLUSIONS

In this work, DES-Si was successfully synthesized and able to remove >95 % of Cu(II) from aqueous solution at an optimum pH of 8, 5 mg L^{-1} of initial concentration of Cu(II), and 45 min of contact time. The removal efficiency of Cu(II) using DES-Si was compared to that using DES-Si in the presence of a ligand. A higher removal percentage was achieved with DES-Si alone, indicating that the addition of the ligand reduced adsorption efficiency. This decrease is attributed to the formation of stable Cu(II) ligand complexes in solution, which reduce the availability of free Cu(II) ions for adsorption. The adsorption mechanism is primarily

governed by electrostatic interactions, surface complexation and possible hydrogen bonding between the Cu(II) ions and functional groups (such as amine and hydroxyl) on the DES-Si surface. The data obtained from adsorption kinetic and isotherm studies showed that the adsorption of Cu(II) onto DES-Si is best fitted with PSO, Langmuir, Freundlich and Temkin models.

SUPPLEMENTARY MATERIAL

Additional data and information are available electronically at the pages of journal website: https://www.shd-pub.org.rs/index.php/JSCS/article/view/13520, or from the corresponding author on request.

Acknowledgement. The authors are thankful to the Ministry of Higher Education Malaysia (FRGS/1/2024/STG04/USM/03/1) for funding this work.

ИЗВОД

СИЛИКА МОДИФИКОВАНА ХОЛИН-ХЛОРИД/УРЕА ДУБОКИМ ЕУТЕКТИЧКИМ РАСТВАРАЧЕМ ЗА АДСОРПЦИЈУ Cu(II) БЕЗ ЛИГАНДА

SAMER S. ABURUB[1,2], NUR FARAHIN AB MANAF[1], ASMAA' M. ROHISHAM[1],NUR NADHIRAH MOHAMAD ZAIN[3], NORAZZIZI NORDIN[1] и NURUL Y. RAHIM[1]

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У овој студији синтетисана је силика модификована хидрофилним дубоким еутектичким растварачем (DES) састављеним од холин-хлорида и урее (DES-Si) и испитана за уклањање Cu(II) јона из водених раствора без употребе лиганада. DES-Si је успешно окарактерисана применом инфрацрвене спектроскопије са Фуријеовом трансформацијом, термогравиметријске анализе, нуклеарне магнетне резонанце и елементалне анализе, чиме је потврђена ефикасна имобилизација DES на површини силике. Експерименти адсорпције у шаржном режиму показали су да DES-Si остварује ефикасност уклањања Cu(II) већу од 95 % под оптималним условима (pH 8, почетна концентрација Cu(II) 5 mg L^{-1}, време контакта 45 min, 25 °C). Максимални адсорпциони капацитет добијен из Langmuir модела износио је 17,54 mg g^{-1}, што указује на снажан афинитет према Cu(II) јонима. Кинетичка испитивања показала су да процес адсорпције прати модел псеудо--другог реда (R^2 = 0,9964), што сугерише да је брзина процеса одређена површинским интеракцијама. Равнотежни подаци добро су описани Langmuir, Freundlich и Temkin изотермним моделима, при чему је Temkin модел показао најбоље слагање са експерименталним подацима (R^2 = 0,9914). Упоредне студије показале су да је уклањање Cu(II) помоћу DES-Si без хелатног лиганда значајно ефикасније него у присуству 1,10-фенантролина, што потврђује ефикасност адсорпције без лиганада. Ови резултати указују да је DES-Si обећавајући и еколошки прихватљив адсорбент за ефикасно уклањање Cu(II) из водених медијума.

(Примљено 29. августа, ревидирано 20. новембра 2025, прихваћено 20. фебруара 2026)

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Journal of the Serbian Chemical Society
JSCS@tmf.bg.ac.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 91 (0) S1–S4 (2026) *Supplementary material*

SUPPLEMENTARY MATERIAL TO

Silica modified with choline chloride/urea DES for ligand-free Cu(II) adsorption

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J. Serb. Chem. Soc. 91 (0) (2026) 000–000

The equation for pseudo-first order (PFO) is described as follows:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \text{(S-1)}$$

where k_1 is the rate constant of the pseudo-first-order model (min^{-1}), q_e is the amount of metal adsorbed at equilibrium (mg g^{-1}), and q_t is the amount of metal adsorbed at time t (mg g^{-1}). The value of k_1 and q_e was obtained from the plotted graph of $\log(q_e–q_t)$ against t.

Pseudo-second-order (PSO) equation by Ho and Mckay (1999) is as followed:

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

where k_2 is the rate constant of pseudo-second order (g mg^{-1} min^{-1}). A graph of t/q_t *vs* t was plotted to find the initial adsorption rate, h (mg g^{-1} min^{-1}), and the half-equilibrium time, $t_{½}$ (min).

$$h = k_2 q_e^2 \quad \text{(S-3)}$$

$$t_{1/2} = \frac{k_2}{q_e} \quad \text{(S-4)}$$

The Langmuir isotherm describes the monolayer adsorption of an adsorbate onto the surface of an adsorbent containing a finite number of active sites. There will be no further sorption once an active site is filled up and the surface reaches a saturation point where the maximum adsorption is achieved.

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The isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{bq_m} \quad \text{(S-5)}$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_m is the adsorption capacity (mg g^{-1}), and b is the rate of adsorption (L mg^{-1}). The features of the parameter for Langmuir adsorption isotherm can be used to predict the affinity between the adsorbate and adsorbent using a dimensionless constant called the separation factor or equilibrium parameter (R_L), which is expressed by the following relationship:

$$R_L = \frac{1}{1 + bC_0} \quad \text{(S-6)}$$

Where C_0 is the initial adsorbate concentration (mg L^{-1}), R_L stipulates the favourability of the adsorption nature, either irreversible (R_L = 0), favorable ($0<R_L<1$), linear (R_L = 1) or unfavorable (R_L > 1). The values of linear regression coefficient (R^2) is 0.9887, demonstrating that the experimental data fitted well with the Langmuir isotherm equation. The R_L value in the present investigation was found to be 0.0911, indicating that the adsorption of the Cu (II) ions onto DES-Si is favorable, with the maximum adsorption capacity (q_m) of 17.54 mg g^{-1}.

The Freundlich isotherm describes the heterogeneous adsorption between adsorbate and adsorbent with a non-uniform distribution of heat of adsorption. The Freundlich isotherm is represented by the following Equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad \text{(S-7)}$$

Adsorption capacity, K_F, (mg g^{-1}) and Freundlich exponent, n can be found by plotting graph of log q_e versus log C_e. The n value indicated the type of sorption process to be chemical process if n <1 and physical process if n >1. As shown in Table V, it can be found that the value of R^2 is 0.976. In the present study, since n value is larger than 1, it indicates the physical adsorption of Cu (II) ions onto DES-Si.

The Temkin isotherm is a model that assumes the heat of adsorption (function of temperature) of the adsorbate in the layer would decrease linearly with the surface coverage due to adsorbent–adsorbate interactions. The equation of Temkin model is written as:

$$q_e = \frac{RT}{b_T} \ln S_T + \frac{RT}{b_T} \ln C_e \quad \text{(S-8)}$$

Where b_T (J mol^{-1}) is the Temkin constant related to the heat of adsorption and S_T (L g^{-1}) is the Temkin isotherm equilibrium binding constant. As shown in

Table V, it can be found that the value of R^2 is 0.9914, suggesting that these experimental data fit very well with the Temkin isotherm model. The following values were estimated: S_T = 6.4887 L g^{-1}, b_T = 711.17 J mol^{-1}, which are indications of the heat of sorption and physical adsorption process, respectively.

Dubinin-Radushkevich isotherm is a model that is commonly used to describe the mechanism of adsorption onto a heterogeneous surface and can be applied to determine the mean of adsorption energy (E) of the adsorbate. This adsorption energy is used to remove the adsorbate from the sorption space using the equation below:

$$E = \frac{1}{\sqrt{2\beta}} \tag{S-9}$$

where β is the DR model constant (mol^2kJ^{-1}). The value of E is important as it can be used to determine the type of adsorption of metal ions, either physical or chemical adsorption. The linear equation of this model is represented as:

$$\ln q_e = \ln q_m - \beta E^2 \tag{S-10}$$

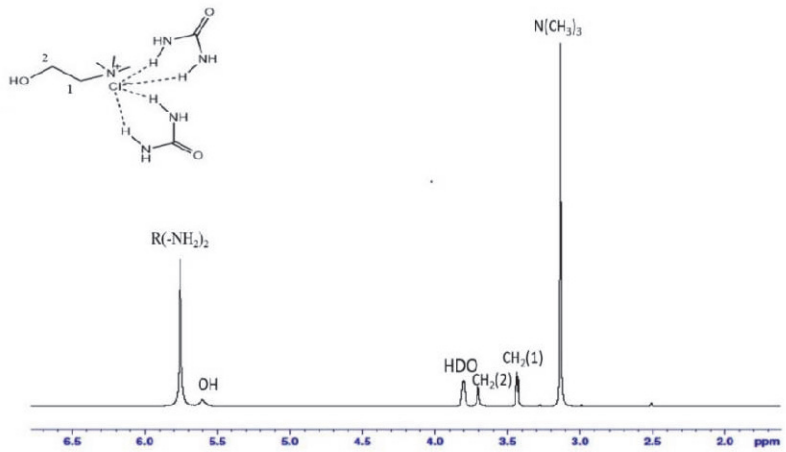

Fig. S1(a) ^{1}H-NMR spectrum of DES

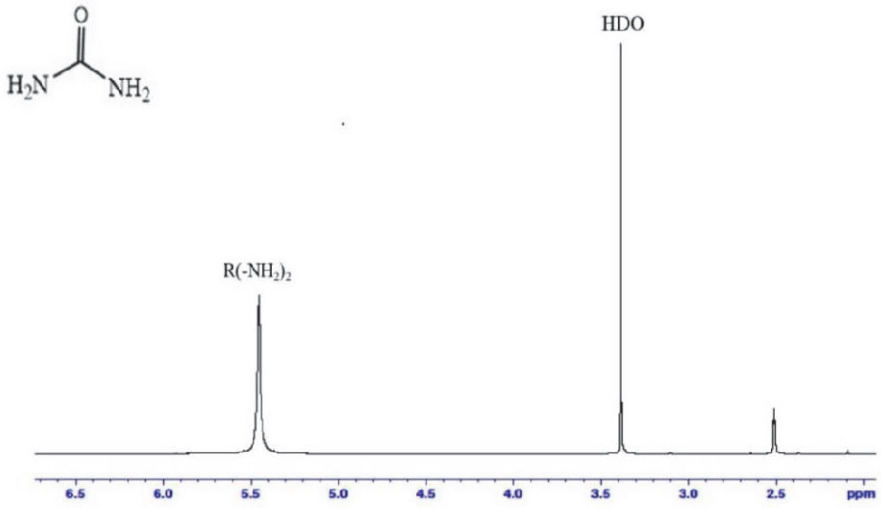

Fig. S1(b) ^{1}H-NMR spectrum of urea

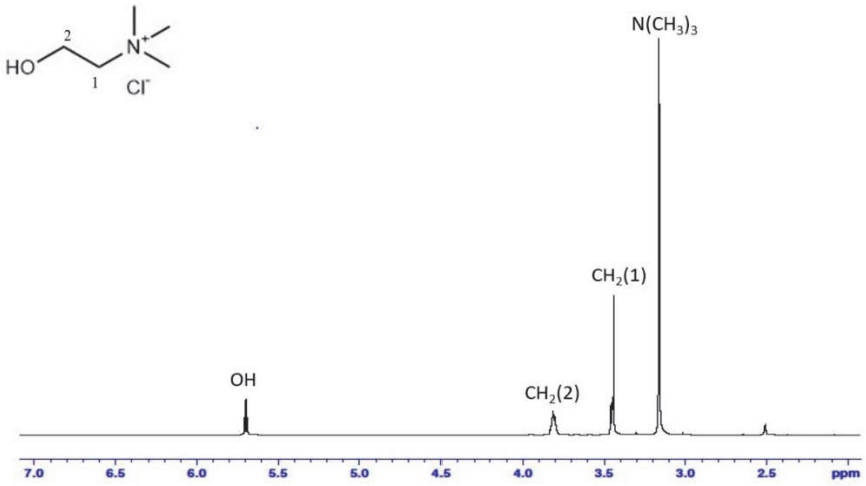

Fig. S1(c) ^{1}H-NMR spectrum of choline chloride.