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

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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 (Cu(II)) is a metal known for its excellent thermal and electrical conductivity, ease of fabrication, and good corrosion resistance. As a result, it is

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widely used in 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 defence, 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 selectivities, 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 liquid (ILs) modified silica were successfully applied as stationary phases of liquid chromatography and adsorbents.[13] However, it is challenging for preparing the 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 is ionic liquids analogues were introduced.[15] DESs are formed by mixing of hydrogen bond acceptor (HBA) and hydrogen bond donor (HBD) at certain ratio and temperature.[15] DES appear to show useful properties such as easily prepared with high purity, nontoxic, inert with water, and biodegradable.[15] The properties of DESs can be customized to a particular type of chemistry.[15] Owing to these attractive characteristics, attentions had been given to DES as an alternative environment friendly solvents and media for organic and inorganic reactions and separations.[16]

In recent year, DES-based mesoporous silica was explored as alternative stationary phases and adsorbents for the columns of size exclusion chromatography.[17] However, their application as adsorbents for heavy metal

removal particularly Cu(II) remains underexplored. In this study, the feasibility of DES-modified silica (DES-Si) was investigated for Cu(II) removal from aqueous solutions. 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 comparison, the removal of Cu(II) was construct using DES-Si with the presence of 1,10-phenanthroline (phen) in aqueous solution. The optimum condition such as pH, contact time and initial concentration of Cu(II) had been investigated to obtain the efficient removal. In addition, the kinetic and isotherm studies were also determined to identify the mechanism of adsorptions.

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%, Switzerland). Choline chloride (ChCl) was acquired from Sigma-Aldrich (≥98%, St. Louis, MO, USA). 1, 10- phenanthroline monohydrate (phen) was obtained from Systerm Chemicals (Shah Alam, Selangor, Malaysia). Ultrapure water Type I was filtered from ultrapure water system (Division of Millipore, USA).

Instrumentations

The Fourier transform infrared spectroscopy (FT-IR) were obtained from Systerm 2000 PerkinElmer set the wavenumber between 400 and 4000 cm^{-1} at scan rate of 8 scans per min. The thermogravimetric analysis (TGA) was collected from PerkinElmer STA 6000. Nuclear magnetic resonance (NMR) spectrum was analysed using 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 fully computer-controlled Perkin Elmer 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 molar ratio, followed by constant heating and stirring at 80 °C for 2 hours until a clear homogeneous liquid was obtained.[19] Silica has been activated to react with DES. The synthesis scheme of DES and DES-Si was shown in Fig. 1a and 1b respectively. The crude product of DES-Si was obtained by heating at 80℃ for 15 h. Then, the DES-Si was filtered, washed with ultrapure water to remove impurities and unreacted DES before dry at 100℃ for 6 h. Both of DES and DES-Si were characterized using FT-IR, TGA, NMR and elemental analysis.

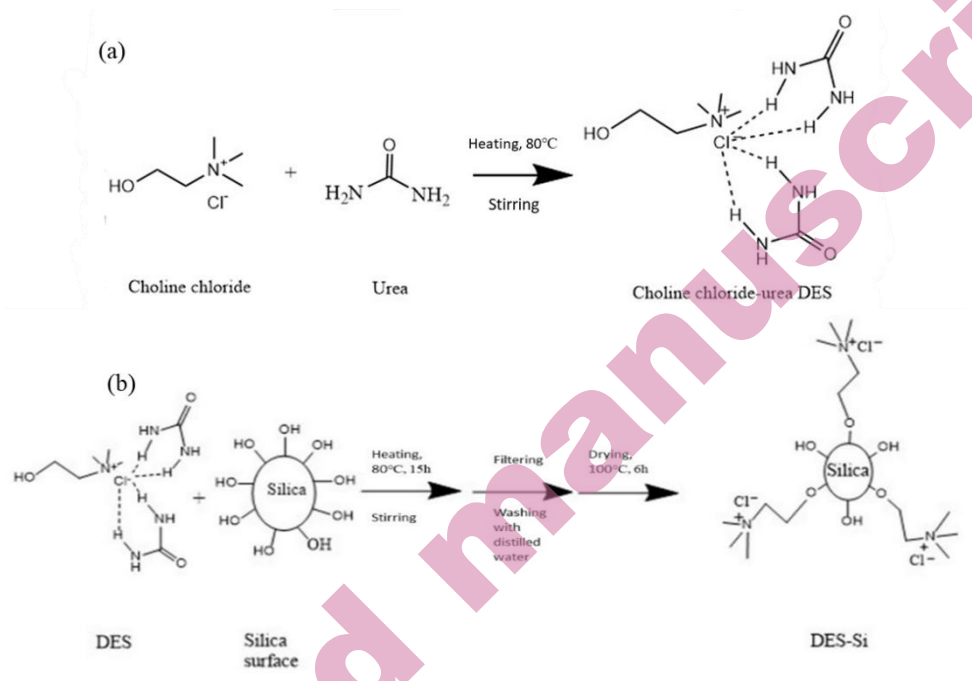

Fig. 1 Synthesis scheme of (a) DES and (b) DES-Si

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 were prepared with concentration of 1, 2, 3, 4 and 5 mg L^{-1} diluted with ultrapure water from 100 mg L^{-1} solution. 100 mg L^{-1} of Cu(II) working solution was prepared in 100 mL volumetric flask by dissolving $CuSO_4.5H_2O$ with ultrapure water.

Optimization parameters for removal of Cu(II) ions

Effect of pH

A series of Cu(II) working solutions (20 mg L^{-1}) were 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 minutes (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 1,10-phenanthroline (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 minutes) at 25 °C using vortex and centrifuge. The solutions were filtered and analysed using AAS. Meanwhile, 0.01 M of phen was added to each of Cu(II) solutions at optimum pH and centrifuged the solutions for various interval times.

Effect of initial concentration

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

RESULTS AND DISCUSSION

Characterization

FT-IR

The FT-IR spectra show various absorption peaks, which indicates different types of 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 to ChCl, such as ν_{as} OH, δ_{as} OH, ρ CH_3, ρ CH_2, ν C-O, ν_{as} CCO and ν_s N-CH_3 in 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 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} NH_2, Si-O-C and Si-O-Si strong absorption bands, ν_{as} CCO and ν_s N-CH_3, at 3460, 1639, 1103, 970 and 802 cm^{-1}, respectively. The presence of these peaks confirms the attachment of DES with the activated silica.[19] The spectrum for activated silica shows the existence of bands associated to Si-O-Si and OH at 1099 and 3441 cm^{-1}, respectively. These bands indicate the presence of active site on activated silica where modification process can occur.[21]

TGA

TGA analysis was carried out to study the decomposition pattern of DES and DES-Si. The TGA analysis for all compounds were shown in Fig. 3. For the DES sample, TGA show the first composition at 61°C dues to the loss of water. Meanwhile, there were composition of ChCl and urea at 220 °C and 306 °C, respectively.[22] After immobilized onto the silica, the weight of DES-Si did not change significantly, thus make it stable at high temperatures. The total weight loss of DES-Si upon increasing the temperature from 250 to 700 °C was less than 2% due to the desorption of water and the degradation of organic components before performing TGA.[19] Therefore, only a small amount of fly ash was released from the compounds in the TGA analysis.

Table I Wave numbers and their assignment for FT-IR spectra

Assignments	Wave number (cm^{-1})	
	DES	DES-Si
δ_s NH_2,	1663	
ν C=O	1608	
δ_{as} OH	3025	
δ_{as} NH_2		1639
ρ CH_3	1476	
ρ_s NH_2	1433	
ν_{as} CN	1169	
Si-O-Si, Si-O-C		1103
ρ CH_2	1082	
ν C-O	1005	
ν_{as} CCO	952	970
ν_s N-CH_3	865	
ω C = O	783	
ν_s N-CH_3		802
δ N-H	692	

ν = stretching; δ = bending; ρ = rocking; ω = weak

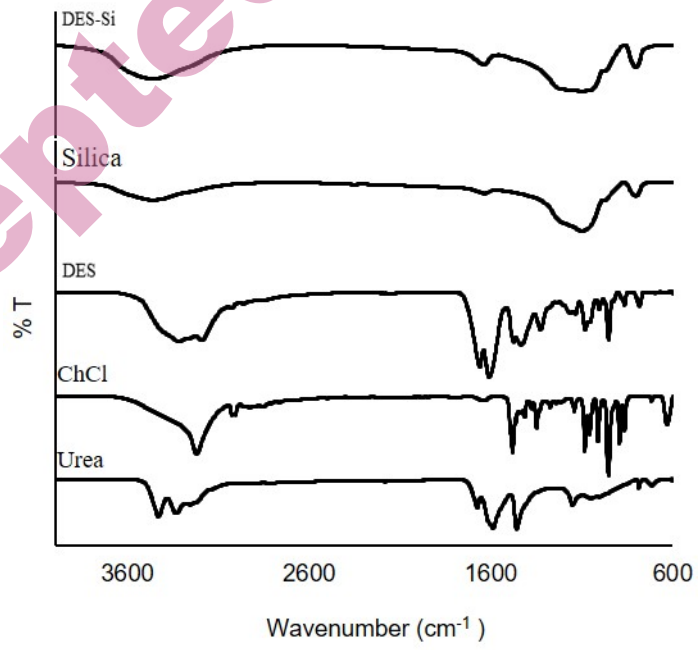

Fig. 2 FT-IR spectra for urea, ChCl, DES, activated silica and DES-Si

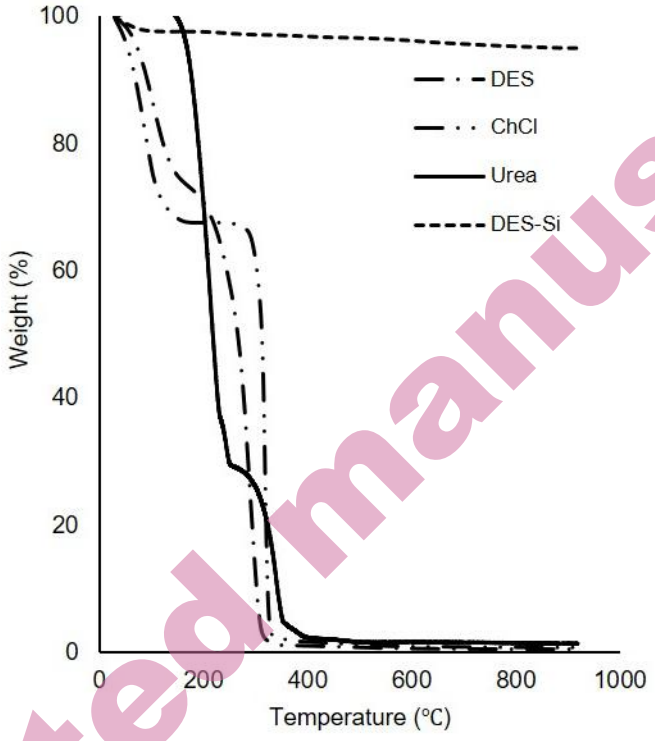

Fig. 3 TGA analysis of urea, ChCl, DES, and DES-Si

NMR

The structure and spectra of DES, urea and ChCl were deduced from ^{1}H-NMR (refer supplementary Fig. S1(a-c)) with tabulated assignment of functional groups in Table II. The spectrum of DES (Fig. S1(a)) consisted of multiplet peaks for the NH_2 (δ=5.76 ppm, 8H) and a singlet peak for the deuterium hydroxide oxide (HDO) (δ=3.70, 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 singlet peak for the OH (δ=5.60, 1H), multiplet peaks for CH_2 (δ=3.80, 2H; δ=3.43, 2H) and multiplet peaks for $(CH_3)_3$ (δ=3.14, 9H).

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 is confirmed that the DES was successfully immobilized onto silica. The detection of small amount of nitrogen and carbon in silica may be due to contamination during the preparation for analysis that led to the adsorption

of impurities onto the surface of silica. 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 porosity and structural integrity of the silica support.

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

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

Sample	Element (%)		
	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

Optimization parameters for removal of Cu(II)

The percentage removal of Cu(II) was calculated using this equation:

$$\% \text{ removal} = \frac{(C_o - C_e) \times 100}{C_o} \quad (1)$$

where C_o is the initial adsorbate concentration (mg L^{-1}) and C_e is the equilibrium concentration of the adsorbate (mg L^{-1}).

Effect of pH

The pH of the metal solution plays a crucial role in adsorption studies. In this experiment, the removal of Cu(II) using DES-Si and DES-Si-phen was carried out over a pH range of 1 to 8. The removal of Cu(II) (Fig. 4), with and without ligand, was found to increase as the pH of the solution increased from 4 to 8. This result indicates that the removal of Cu(II) using DES-Si is favoured under alkaline conditions. At lower pH, the concentration of H_3O^+ ions greatly exceed that of

Cu(II), leading to competitive binding at the active sites on DES-Si. At higher pH, the concentration of H_3O^+ ions are lower, allowing a greater number of Cu(II) ions to bind to the surface. The adsorption mechanism primarily involves electrostatic interactions and surface complexation between divalent Cu^{2+} ions and negatively charged functional groups present on the DES-modified silica surface. These interactions are more favourable at higher pH values, where proton competition is reduced. The H_3O^+ ions are replaced by metal ions and metal species such as Cu^{2+}, $CuOH^+$, and $Cu_2(OH)_2^{2+}$. However, an increase in pH may also promote the precipitation of Cu(II) as metal hydroxides. In this study, the pH was adjusted to 8, and precipitation was monitored throughout to ensure it did not occur. The solution at pH 8 was confirmed to be free from precipitation. Based on Fig. 4, the removal efficiency of Cu(II) using DES-Si reached 83.67%, compared to 55.52% for DES-Si-phen at the same pH. Therefore, the optimal pH for Cu(II) adsorption in this system is pH 8.

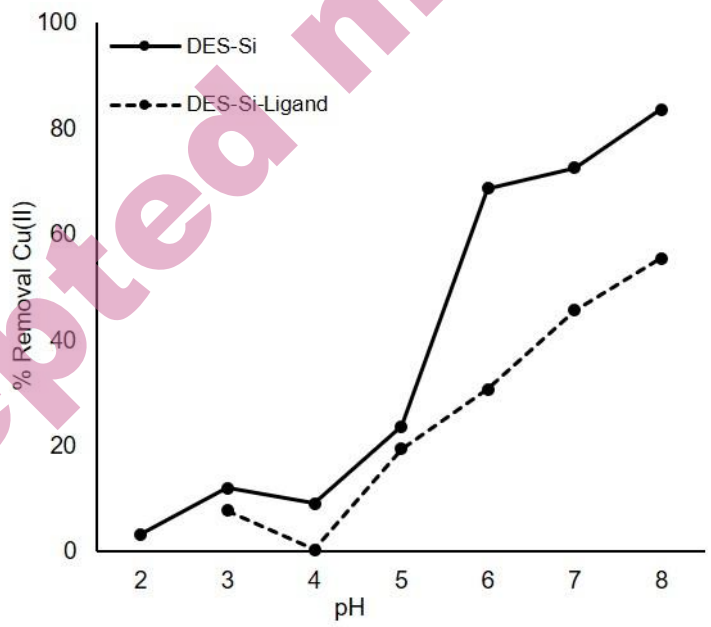

Fig. 4 Effect of pH on adsorption of Cu(II) (Condition: sorbent: 50 mg; initial concentration: 30 mg L^{-1}; volume: 20 mL; contact time: 30 min; temperature: 25 °C)

Effect of contact time

The contact time ranges from 5 to 45 min were investigated for removal of Cu(II) using DES-Si and DES-Si-phen. The result in Fig. 5 shows that the removal percentage is increased with increasing the contact time using DES-Si and DES-Si-phen. The percentage removal of Cu(II) was slightly constant from 5 min and

increase 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 are 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^2 (II) ions are available to bind to the DES-Si surface. These Cu–phen complexes might also have different charges or shapes that make them less likely to interact with the functional groups on DES-Si. As a result, the presence of phenanthroline interferes with the adsorption process instead of helping it. The optimum contact time of 45 min was used for the next optimization for removal of Cu(II).

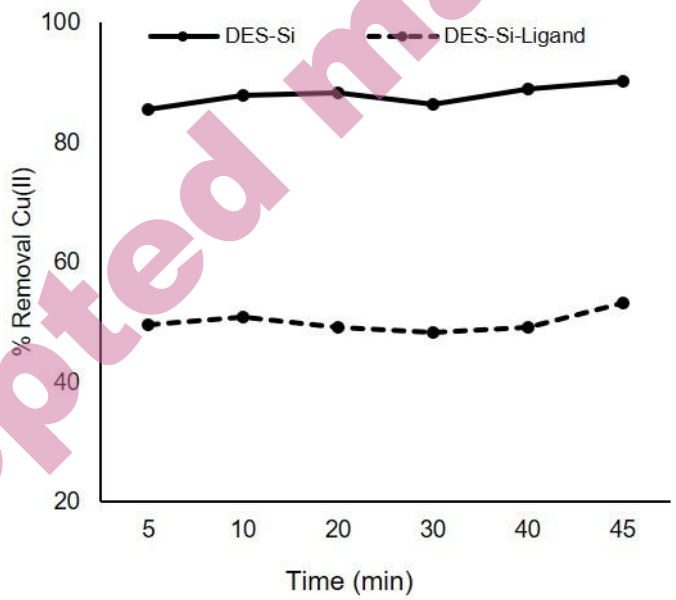

Fig. 5 Effect of contact time on adsorption of Cu(II) (Condition: pH: 8; sorbent: 50 mg; initial concentration: 30 mg L^{-1}; volume: 20 mL; temperature: 25 °C)

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 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.

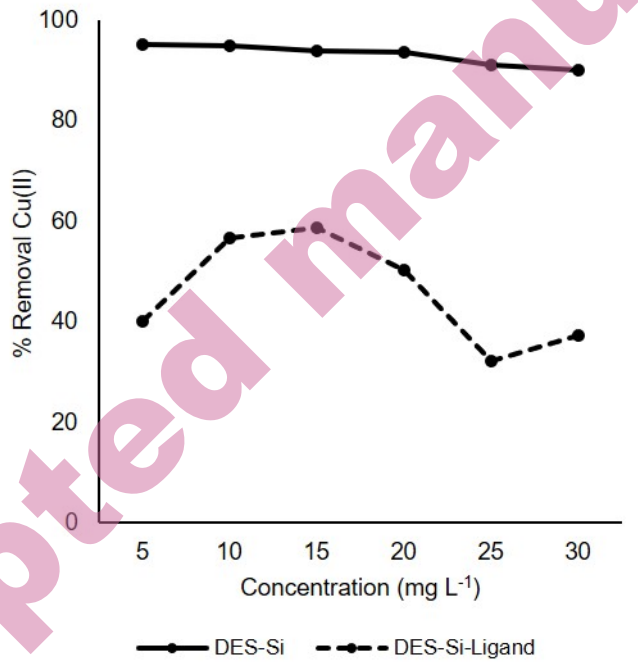

Fig. 6 Effect of initial concentration of Cu (II) (Condition: pH: 8; sorbent: 50 mg; contact time: 45 min; volume: 20 mL; temperature: 25 °C)

Batch adsorption studies

Adsorption kinetic

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

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (2)$$

where k_1 is the rate constant of 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)[26] is as followed:[8]

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (3)$$

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

$$h = k_2 q_e^2 \quad (4)$$

$$t_{1/2} = \frac{k_2}{q_e} \quad (5)$$

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 kinetic of adsorption. The smaller the value of Δq (%) and RE (%) indicates 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 of experimental data is followed the PSO involving chemisorption mechanism. In this mechanism, the adsorption process is driven by a chemical reaction occurring 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)	6.604	3.776
	$q_{e,calc}$ (mg/g)	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)	6.333	3.560
	k_2 (g/ mg min)	-2.899	0.3933
	h (mg/g min)	-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

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

The Langmuir isotherm describes the monolayer adsorption of an adsorbate onto the surface of an adsorbent containing a finite number of active sites.[8] 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.

The isotherm is represented as:

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{bq_m} \quad (6)$$

where C_e is the equilibrium concentration of the adsorbate (mg L^{-1}), q_m is adsorption capacity (mg g^{-1}) and b are rate of adsorption (L mg^{-1}). The features of parameter for Langmuir adsorption isotherm can be used to predict the affinity between the adsorbate and adsorbent using a dimensionless constant called separation factor or equilibrium parameter (R_L), which is expressed by the following relationship[8]:

$$R_L = \frac{1}{1+bC_o} \quad (7)$$

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), favourable ($0<R_L<1$), linear (R_L = 1) or unfavourable (R_L > 1).[26] 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 favourable with the maximum adsorption capacity (q_m) of 17.54 mg g^{-1}.

The Freundlich isotherm describe the heterogeneous adsorption between adsorbate and adsorbent with a non-uniform distribution of heat of adsorption.[8] The Freundlich isotherm is represented by the following Equation:

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (8)$$

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.[8] 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 heat of adsorption (function of temperature) of adsorbate in the layer would decrease linearly with the surface coverage due to adsorbent–adsorbate interactions.[8] The equation of Temkin model is written as:

$$q_e = \frac{RT}{b_T} \ln S_T + \frac{RT}{b_T} \ln C_e \quad (9)$$

Where b_T (J mol^{-1}) is the Temkin constant related to 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 fitted 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 is an indication for heat of sorption and physical adsorption process, respectively.

Dubinin-Radushkevich isotherm is a model that commonly used to describe the mechanism of adsorption onto a heterogeneous surface[27] and can be applied to determine the mean of adsorption energy (E) of adsorbate. This adsorption energy is used to remove the adsorbate from the sorption space using equation below:

$$E = \frac{1}{\sqrt{2\beta}} \quad (10)$$

Where β is the DR model constant (mol^2 kJ^{-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.[27] The linear equation of this model is represented as:

$$\ln q_e = \ln q_m - \beta E^2 \quad (11)$$

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 and16 kJ mol^{-1}.[24]

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

Isotherm models	Parameter	Temperatue (298K)
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	$_{ST}$ (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

CONCLUSION

In this work, DES-Si was successfully synthesized and able to remove >95% of Cu(II) from aqueous solution at 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 percentage of removal was achieved with DES-Si alone, indicating that the addition of the ligand reduced the 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 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.

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Conflict of Interest: The authors declare that they have no conflict of interest.

И З В О Д

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

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У овој студији синтетисана је силика модификована хидрофилним дубоким еутектичким растварачем (DES) састављеним од холин-хлорида и уреe (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 елементарне анализе, чиме је потврђена ефикасна имобилизација DES-а 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, на 25 °C). Максимални адсорпциони капацитет добијен из Langmuir-овог 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-овим, Freundlich-овим и Temkin-овим изотермним моделима, при чему је Temkin-ов 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.

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