Enhanced removal of Cu(II) from chemically diverse wastewater environment by EDTA-chitosan modified sewage sludge

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ABSTRACT

The removal of Cu(II) from chemically diverse wastewater was studied using a sewage sludgebased adsorbent in which the sewage sludge surface had been functionalized with ethylenediaminetetraacetic acid anhydride (EDTA) and chitosan via a one-step cross-linkage method. The adsorbent was characterized by scanning electron microscope, Fourier transform infrared spectroscopy, thermogravimetric analysis, X-ray diffraction, Brunauer-Emmett-Teller, and X-ray photoelectron spectroscopy. The effect of metal concentration, contact time, changes in pH, ionic environment, presence of competitive ammonia, and recyclability were all investigated. The EDTA-chitosan modified sludge showed good adsorption capacity (42.4 mg g^{-1}) at pH 3.0, which could be ascribed to the attraction between Cu(II) ions and functional groups of the EDTA-chitosan modified sludge surface. The adsorption isotherm data fitted the Langmuir isotherm suggesting that the adsorption process was homogenous. The adsorption equilibrium was reached within 270 min. The kinetics of adsorption followed a pseudo-second-order model, indicating the adsorption of Cu(II) on the surface of EDTA-chitosan modified sludge was due to chelation and ion exchange. The Cu(II) adsorption by EDTA-chitosan modified sludge in a chemically diverse environment including cations and ammonia was excellent. Furthermore, the adsorbent is stable and has good recyclability with more than 27 mg g^{-1} adsorption capacity after several cycles of regeneration, which suggests its suitability in wastewater treatment.

Keywords: Ethylene diamine tetra acidic acid; Chitosan; Sewage sludge; Adsorption

1. Introduction

Ecological contamination by heavy metals represents a significant and long-term hazard to human health as, unlike organic toxins, they are not biodegradable and can bio-accumulate [1]. Cu(II) is an important micronutrient for plants and animals, however, excessive amounts can prove lethal [2]. Cu(II) can be found in the aqueous effluent from many industries, including, for example, electroplating [3], mining [4], printing [5], coloring, iron, and steel generation, nonferrous metal industry [6], and production of dyes [7]. Different approaches have been considered to treat heavy metal-containing wastewater, for example, ion exchange [8], precipitation [9], liquid–liquid extraction [10], oxidation [11], and reduction [12]. However, these wastewater treatment techniques are generally costly and inefficient in terms of removing heavy metal [13]. The treatment process is further complicated due to the usually chemically diverse nature of industrial pollutants. Adsorption is the most attractive approach because of its ease in operation, reproducibility, and selective adsorption of metal ions [14]. The selectivity of adsorption depends on the functional

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groups of the adsorbent, and these may include one or more combinations of amines, amides, carboxylic acids, hydroxyls, thiols, and sulfonic acids [15]. Adsorbents with nitrogen-based functional groups have been shown to be highly effective in selective adsorption of heavy metal ions [16]. Adsorbents previously used for Cu(II) removal from industrial wastewater have included zeolite [17], activated carbon [18], and ion-exchange resin [19].

A by-product of wastewater treatment is sewage sludge. In China, some 82,000 tons of sludge are produced every day from 129 million tons of processed wastewater [20]. The sludge is a cheap source of alumina, silica, and other oxides, and among other uses, is a feedstock in the synthesis of aluminosilicate minerals [21]. It is also used as an adsorbent following surface modifications to change the porosity, surface area, and availability of co-ordinating groups [22].

Chitosan (CS) is a cationic, renewable, and partially deacetylated copolymer of N-acetylglucosamine and glucosamine derived from chitin [23]. It is also biocompatible, bio-renewable, biodegradable, and nontoxic [24]. Furthermore, the abundant availability of amino functional groups on the CS surface represents potential binding sites for heavy metal ion adsorption. However, the hydrophobic nature of CS, means that its application as an adsorbent in wastewater treatment is limited unless the surface can be modified to reduce the hydrophobicity [25].

Ethylenediaminetetraacetic acid (EDTA) is a chelating agent that has been utilized to enhance the ability of natural adsorbents, such as CS [26], CS-silica hybrid materials [27] and mesoporous silica [28]. A number of methods to modify CS have been reported, however, these methods have proved both complex and costly to implement on an industrial scale [29,30]. On the other hand, sewage sludge is a more stable and economic adsorbent but has a limited number of active sites and is unable to achieve high adsorption of Cu(II). However, sewage sludge has a high surface area and an abundance of hydroxyl groups that can be potentially cross-linked with different organic moieties.

In this paper, we describe the synthesis and evaluation of EDTA-CS modified sludge for the adsorption of Cu(II) from diverse industrial wastewaters. The synthesis of EDTA-CS modified sludge preparations is a simple one-pot reaction and makes the carboxyl groups of EDTA and amino groups of chitosan available as the chelating sites for heavy metal adsorption. Adsorbent modification and mechanism of adsorption were characterized by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET), and X-ray photoelectron spectroscopy (XPS). The adsorption performance of this novel adsorbent was also assessed, looking at metal ion concentrations, isothermal adsorption, contact time, the kinetics of adsorption, the effect of pH, and the ionic environment, presence of ammonia, desorption kinetics and recyclability.

2. Materials and experiments

2.1. Materials

Analytical grade chemicals were bought from chemical reagent factory (Xi'an, China). The sewage sludge was sourced from the Fifth Sewage Treatment Plant (Xi'an, China) and was composed of organic matter (52.04%), ash (44.22%) and residual aluminosilicates, and other oxides.

2.2. Synthesis of EDTA-CS modified sludge

The synthesis of EDTA–CS modified sludge is a one-step process in which the CS act as a crosslinking agent between hydroxyl groups of sewage sludge and amino groups of EDTA anhydride (Fig. 1). The obtained sewage sludge sample was washed, filtered, autoclaved at 120°C, and dissolved in 1 M HCl for 10 h. The sludge was again washed several times and freeze-dried overnight [31].

CS was modified with EDTA according to Repo et al. [32]. In brief, CS (1 g) was mixed with 10% (v/v) acetic acid (20 mL) and to this was added methanol (100 mL). Then dried sludge (2 g) was added into the reaction mixture and it is sonicated over a 15 min. EDTA anhydride (3 g) was prepared according to Repo et al. [32], suspended in methanol (100 mL) and added into the mixture over 120 min at 60°C. Stirring at 80 rpm continued for 6 h at 60°C. The mixture was then filtered through centrifuge. The filtered solids were suspended in 200 mL ethanol and stirred for another 6 h at 60°C. Then 0.1 M NaOH solution was used to wash the filtrated, for the removal of unreacted EDTA Finally, the EDTA modified CS was washed with distilled water, 0.1 M HCl, and again with deionized water until pH was neutral. The final product was dried under vacuum at 55°C for 12 h and stored in a desiccator.

2.3. Characterization of materials

The morphology of the sludge surface before and after modification was observed with an SEM (FEI Q45, FEI, USA). Fourier transform infrared (FTIR) spectra (Nexus 870 FTIR; Nicolet, US) was used to determine the functional groups on the surface of the adsorbent. XRD (D/max2200 PC, Rigaku, Japan) was used to analyze the crystal structure. The percentage of the polymer on the EDTA–CS modified sludge was determined by thermogravimetric/differential thermal analyzer (NETZSCHSTA 409 TG–DTA, Germany). The BET surface area and pore size were determined by BET (Gemini VII239, McMurreteak Instrument Co., US). XPS (AXIS SUPRA, Kratos, Britain) was used to analyze the adsorption mechanism of Cu (II).

2.4. Batch study

The capacity of EDTA–CS modified sludge for Cu(II) adsorption was investigated in a batch study using an adsorbent dosage of 0.02 g added to solutions of Cu(II) ions (50 mL) ranging in concentrations from 2.5 to 50 mg L⁻¹. The equilibration time was investigated at a Cu(II) concentration of 30 mg L⁻¹, over a period of 480 min. The pH effect was studied at 30 mg L⁻¹ of Cu(II) concentration from pH 1.0–7.0 with pH adjustments being made with HCl (1 M) and NaOH (1 M). To evaluate the effect of other cations, the experiment was designed with the initial 10 mg L⁻¹ concentration of Cu(II), 0.02 g adsorbent, 2.5–100 mM of co-existing cations in 50 mL volume. The study was designed to assess the Cu(II) removal ability of EDTA–CS modified sludge from a diverse ammonia environment containing 10 mg L⁻¹ Cu(II),



Fig. 1. EDTA-CS synthesis.

0.02 g adsorbent dosage in 50 mL volume with the 2:1–1:16 molar ratios of NH₄–N. In each experiment, 10 mL of solution was filtered by syringe filter (0.45 µm polypropylene), and the concentration of remaining Cu(II) was determined by inductively coupled plasma spectroscopy (ICP–OES; model iCAP 6000 Thermo Electron Corporation, USA). The amount of Cu(II) adsorption by an adsorbent at equilibrium (q_e) was calculated as per Eq. (1), below:

$$q_e = \frac{\left(C_0 - C_e\right)V}{M} \tag{1}$$

where C_0 and C_e represent the initial and equilibrium Cu(II) concentrations (mg L⁻¹) respectively, q_e (mg g⁻¹) is the equilibrium adsorption amount, V (L) represents the volume of Cu(II) solution, and M (g) is the mass of the adsorbent.

2.5. Regeneration study

In the regeneration experiment, the 0.02 g adsorbent loaded with 30 mg L⁻¹ of Cu(II) metal was filtered and washed with 0.1 M HCl (50 mL). The adsorbent was then washed with deionized water to neutral pH. The regenerated adsorbent was used again in the succeeding adsorption-desorption cycles. The desorption kinetics were also determined with 0.1 M HCl (50 mL) volume and samples were taken after different time intervals from 0 to 480 min.

3. Result and discussion

3.1. Characterization

The SEM images of sewage sludge and EDTA–CS modified sludge (Figs. 2a–d) were recorded at a magnification of 5,000 and show significant differences in the surface morphology of the sludge. The unmodified sludge (Figs. 2a and b) is porous and the particles have sharp edges. The crosslinking with EDTA–CS (Figs. 2c and d) resulted in rounded particles with few obvious pores and there is a layer of material that covers the surface of sludge. The assumption was made that these changes are due to the role of EDTA coverage by crosslinking CS with sewage sludge. In the FTIR spectrum of the sewage sludge and EDTA–CS modified sludge (Fig. 3), the peaks appearing at 1,031 cm⁻¹ represent the presence of Si–O–Si or Si–O–C, demonstrating the presence of silicon in the sludge [33]. In the EDTA–CS modified sludge, the peaks at 1,635 cm⁻¹ represent bending vibrations of H–O–H, and the small peaks around 517 cm⁻¹ are due to Al–O–Si bending vibrations [34]. The absorption band at 2,927 cm⁻¹ corresponds to C–H stretching vibrations and the broad stretching peak at 3,444 cm⁻¹ is attributed to the O–H and N–H stretching of the hydroxyl and amino groups of the CS [35]. The peak at 1,163 cm⁻¹ may be assigned to the C–O–C asymmetric vibration of the crosslinking CS glycan [26].

TGA provides information regarding adsorption, desorption, and phase transition, as well as solid–gas reactions, chemisorption, and decomposition. The (TGA) curves of the sewage sludge and EDTA–CS modified sludge are shown in Fig. 4. There was an overall 3% weight loss from 0°C to 600°C and the weight loss from 200°C to 600°C is assigned to the loss of structural water [36]. Above 200°C the organic component of the sludge degrades rapidly with the sludge losing 53.6% weight, and the EDTA–CS modified sludge losing 56.58%. This can be used to estimate the proportion weight of CS crosslinked EDTA on the surface of sludge [37]. The weight proportion of EDTA–CS modified sludge (56.58 wt.%) is higher than unmodified sewage sludge (53.6 wt.%). This provided additional evidence for the modification of the sewage sludge surface with a chelating agent and crosslinking of the CS.

In the XRD analysis (Fig. 5), the characteristic diffraction peaks for SiO₂ and for aluminosilicates were observed at $2\theta = 26.47$ and 21.8, respectively [38], in both the modified and unmodified sludge, demonstrating that the CS cross-linkage to EDTA and sewage sludge had no significant effect on the underlying crystalline structure of the sewage sludge, as has been reported previously [15].

The BET specific surface area and total pore volume of the sewage sludge (1.4425 m² g⁻¹ and 0.005997 cm³ g⁻¹, respectively) and EDTA–CS modified sludge (0.7779 m² g⁻¹ and 0.004545 cm³ g⁻¹, respectively) were determined. The decreased specific surface area and pore volume of the modified sewage sludge is consistent with the CS cross-linked EDTA modification and as previously reported [32,37].



Fig. 2. Scanning electron microscope micrographs of the sewage sludge (a and b) and EDTA-CS modified sludge (c and d).



Fig. 3. FTIR spectra of the sewage sludge and EDTA-CS modified sludge.

3.2. Batch study

3.2.1. Effect of pH

The pH of the aqueous solution determines the surface charge of the adsorbent and in turn the metal speciation [39] and is thus the rate determining factor of the adsorption



Fig. 4. Thermogravimetric analysis curve of the sewage sludge and EDTA–CS modified sludge.

process. It is therefore important to know the ionic state of the adsorbent functional groups as well as the metal ion solution chemistry at different pH. At lower pH, with higher concentration of H^+ ions in solution, the adsorbent surface will be protonated ($-NH_3^+$ and -OH) and at neutral pH, deprotonated ($-NH_2$ and -OH), changing the adsorp



Fig. 5. X-ray-diffraction analysis of the sewage sludge and EDTA–CS modified sludge.

tive capacity of the surface for positively charged metal ions.

The adsorption capacity (q_e) of EDTA–CS modified sludge for Cu(II) vs. the initial solution pH plot is shown in Fig. 6. The study of Cu(II) ion adsorption was limited to pH range of 2.0–6.0 as at pH > 6.0, Cu(II) ions are precipitated as hydroxides, Cu(OH)⁺, Cu(OH)₂, Cu₂(OH)²⁺, Cu(OH)⁻₃ [40]. The absorption capacity, $q_{e'}$ increased sharply in the 2.0– 3.0 pH range to a maximum at pH 3.0 and decreased slightly thereafter to pH 6.0. The relatively lower adsorption of copper at pH 2.0 is due to competition for adsorption sites between the hydrogen and Cu(II) ions and the electrostatic repulsion of the –NH⁺₃ moiety [1]. At pH 3.0, the adsorbent surface is increasingly deprotonated and metal co-ordination with –NH₂ and –OH becomes favored.

3.2.2. Initial concentration influence

The absorptive capacity of sewage sludge and EDTA-CS modified sludge were compared over a range of different initial concentrations of Cu(II) metal ions (Fig. 7) after adjustment of the solution to pH 3.0. The data shows the active sites of the sewage sludge and the EDTA-CS modified sludge are saturated at 2.9 and 42.4 mg g⁻¹ Cu(II), respectively. The effect of the initial concentration of metal ions can be explained in two steps. At the first stage, the active sites of the adsorbent were not saturated, and the equilibrium adsorption capacity increased with the increase in concentration. While at the second stage, the equilibrium adsorption capacity remains unchanged with the increase in concentration. The concentration of ions provides the driving force behind the transfer of ions mass in a solid and aqueous phase until the maximum adsorption capacity attained. The EDTA-CS modified sludge was clearly a superior Cu(II) adsorbent when compared to raw sewage sludge (Fig. 7) and also to other previously studied adsorbents listed in Table 1.



Fig. 6. Effect of initial pH of aqueous solution on the adsorption of Cu(II) by EDTA–CS modified sludge.



Fig. 7. Adsorption capacity of sewage sludge and EDTA–CS modified sludge was compared over a range of initial Cu(II) concentrations.

3.2.3. Adsorption isotherm

The adsorption isotherms provide vital information about the adsorbate distribution between the liquid and phase, which is essential to understand the adsorption mechanism [14]. Two isotherm models, that is, Langmuir and Freundlich [24], were applied to the data to describe the metal ions equilibrium of adsorption on the adsorbent. The monolayer adsorption on the homogenous structured adsorbent attributes to Langmuir isotherm, with no affinity between the adsorbates and active sites. The following Eq. (2) represents the Langmuir isotherm:

$$\frac{1}{q_e} = \frac{1}{bq_m C_e} + \frac{1}{q_m}$$
(2)

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Table 1 Comparison of adsorption capacities for Cu(II) metal ions between different modified adsorbents reported in the literature

Material	Adsorption amount (mg g ⁻¹)	Optimum pH	Reference
Modified bagasse pulp cellulose	35.2	5.0	[41]
Sugarcane bagasse modification by tetraethylenepentamine	16.6	3.0	[42]
Caryota urens seeds surface modification by alkali	27.3	6.0	[43]
Modified brown algae Padina sanctae-crucis biomass	13.9	6.0	[44]
Cucurbita moscha modified by alkali	27.7	6.0	[45]
Ramie stalk modification by amino	37	5.0	[46]
EDTA-chitosan modified sewage sludge	42.4	3.0	This study

where C_e (mg L⁻¹) and q_e (mg g⁻¹) are the equilibrium concentration and adsorption capacity of the adsorption process, respectively, while *b* (L mg⁻¹) is the constant of adsorption equilibrium. The Freundlich isotherm depicts in Eq. (3), the adsorption on the heterogeneous surface of the adsorbent, on which adsorption raises with an increase in the concentration of solute [24].

$$\log q_e = \frac{1}{n} \log C_e + \log k_f \tag{3}$$

where n and k_f are the Freundlich isotherm constants and affiliated to the intensity and the adsorption capacity accordingly.

Table 2 shows the obtained values of Langmuir and Freundlich isotherms constants and their correlation coefficients. The Langmuir isotherm model is a better fit than the Freundlich isotherm, as demonstrated by the higher regression correlation, $R^2 > 0.982$. Also the experimental maximum adsorption capacity was close to the calculated value, thus supporting a homogeneous monolayer model for the adsorptive process [47].

3.2.4. Influence of contact time

The influence of contact time on the adsorption of Cu(II) by EDTA–CS modified Sludge is shown in Fig. 8. with rapid initial Cu(II) adsorption which then slows before reaching equilibrium. At the beginning of the adsorption process, rapid adsorption took place due to plenty of available active sites, then it slowed down because of the less availability of active sites and a decrease in Cu(II) concentration in aqueous solution. The maximum uptake of Cu(II) at 270 min. Therefore, the contact time of 480 min is sufficient to attain equilibrium for the Cu(II) adsorption at high metal ion concentrations, which was chosen for further studies. This compares favorably to previous reports from Zhang (24 h) [47] and Li (7 h) [48].

3.2.5. Adsorption kinetic parameters

The adsorption kinetics is an important parameter to determine the adsorption rate of Cu(II) metal. The data was fitted to pseudo-first-order and pseudo-second-order models. Eq. (4) represents the pseudo-first-order [24].

$$\ln\left(q_e - q_t\right) = \ln q_e - k_1 t \tag{4}$$

The pseudo-second-order model is represented in Eq. (5).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(5)

where q_t and q_e (mg g⁻¹) describe as the quantity of Cu(II) adsorbed on the adsorbents (mg g^{-1}) at time t (min) and at equilibrium time, respectively. k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constants of the pseudo-first-order model and pseudo-second-order model, respectively. The calculated kinetic parameters (Table 3) and the graphs of the kinetic models (Fig. 9) suggest that the pseudo-second-order model is the best fit to the adsorption experiment with a regression correlation (R^2) of 0.995, rather than the first-order model, with an R^2 value of 0.953. Also, the calculated q_a value from the pseudo-second-order model is comparable to the experimental q_e value, indicating that the adsorption process for EDTA-CS modified sludge was chemical. The results are also indicative of chemical bonds being formed during the process due to electron transfer, sharing, or relocation. These results are in accord with previous work [11].

3.3. Competition for absorption by other cations

Monovalent and divalent cations, such as Na⁺, K⁺, Ca²⁺, and Mg2+ are also commonly found in industrial wastewater and these cations are likely to compete with the heavy metals for active sites in the adsorption process. The effect of cation competition on the ability of EDTA-CS modified sludge to adsorb Cu(II) are shown in (Fig. 10). It can be seen there was a negligible effect on Cu(II) adsorption, even at a very high concentration of cations (up to 100 mmol L⁻¹). The preferential adsorption of Cu(II) must be due to its higher coordination ability with the amine groups of the EDTA functionalized adsorbent. Such preference for Cu(II) in the presence of competing cations has been reported previously for EDTA-functionalized bamboo activated carbon [49]. It can be seen that complexation between Cu(II) and EDTA-CS modified sludge was stronger than other monovalent or divalent co-existing cations. As compared with the monovalent Na⁺ and K⁺, the divalent Ca²⁺ and Mg²⁺ have a little influence on the removal of Cu(II) because of the high binding constant

Adsorbent	Parameter	Parameters of Freundlich isotherm				
	$q_{\rm max} ({ m mg} { m L}^{-1})$	<i>b</i> (L mg ⁻¹)	R^2	п	k _f	R^2
EDTA-CS modified Sludge	40.95	2.236	0.982	3.718	19.37	0.839

Table 2 Freundlich and Langmuir adsorption model parameters of Cu(II) adsorption on EDTA–CS modified sludge



Fig. 8. Effect of contact time of Cu(II) metal aqueous solution with EDTA–CS modified sludge (metal concentration 30 mg L^{-1} , 0.02 g adsorbent; pH = 3.0).

with EDTA than monovalent cations. The EDTA–CS modified sludge showed high attraction towards the Cu(II) and it could be removed selectively under the influence of co-existing ions, which could be because of EDTA modification on the sewage sludge surface.

3.4. Effect of competitive ammonia NH₄

The wastewater from different industries often contains ammonia which can complex with Cu(II) and other metals present in the wastewater. The Cu(II) ammonia complexes are not easy to separate and are quite stable in solution, which causes difficulty in the selective adsorption of Cu(II) from this complex wastewater system. The capacity of the adsorbent for binding Cu(II) in the presence of ammonia was tested using a range of different Cu(II) to ammonia ratios. As can be seen in Fig. 11, the presence of higher levels of ammonia (up to 1:16 molar ratio NH₄–N) resulted in only a small decrease in the adsorbence of Cu(II) by the EDTA–CS modified sludge. These results may be explained by a previous report of the stability (pk-value) of co-ordinated Cu(II) metal

Table 3 Parameters of kinetic models of Cu(II) ion adsorption by the EDTA–CS modified sludge

$C_0 ({ m mg} { m L}^{-1})$	$q_{\rm exp} ({ m mg}{ m g}^{-1})$	Pseudo-first-order			Pseudo-second-order		
		$k_1 ({\rm min}^{-1})$	$q_{\rm cal} ({ m mg}~{ m g}^{-1})$	R^2	$k_2 [g/(mg min^{-1})]$	$q_{cal} ({ m mg \ g^{-1}})$	R^2
30.2	42.65	3.72 × 10 ⁻³	23.99	0.953	1.75 × 10 ⁻³	42.84	0.995



Fig. 9. Kinetic models fitting for the Cu(II) adsorption on the EDTA–CS modified sludge (a) pseudo-first-order and (b) pseudo-second-order.



Fig. 10. Effect of coexisting cations on Cu(II) adsorption (10 mg L^{-1}) onto absorbent (0.02 g mg) while varying the concentration of an additional cation over a concentration range of 2.5–100 mmol L^{-1} .

ions being increased with a higher number of amine groups in the chelating agent [42].

3.5. Stability and regeneration

For the adsorbent to be reused it is important to be able to fully desorb the Cu(II). This was successfully achieved (Fig. 12a) using 0.1 M HCl over 60 min. We then determined the performance of the EDTA–CS modified sludge after being recycled four times (Fig. 12b). The adsorption of Cu(II) after the first cycle of regeneration decreased from 39.97 to 35.88 mg g⁻¹ and after four rounds of recycling had decreased to 27 mg g⁻¹. It should be noted that the performance of the adsorbent after the fourth cycle was still better than that previously reported [15]. In the desorption process, some functional sites of the adsorbent could be destroyed and were not able to recover in the repeated cycles.



Fig. 11. Effect of ammonia on Cu(II) adsorption (metal ion concentration 10 mg L⁻¹, 2:1–1:16 molar ratio of NH_a).

3.6. XPS analysis and adsorption mechanism

The XPS spectra of the sludge, EDTA-CS modified sludge, and EDTA-CS modified sludge-Cu(II) were compared (Fig. 13a). The C content decreased from 70.48% to 58.39%, while the N content increased from 4.10% to 5.71%, and O increased from 23.32% to 32.17%. Adsorbed Cu(II) content of 0.37% was observed after the adsorption process. In the XPS spectra of the adsorbed Cu(II) (Fig. 13b) 4s and 4p absorption peaks, a new peak at around 933 eV was attributed to Cu 4f, characteristic of bound Cu(II) on the EDTA-CS modified sludge surface. This was confirmed by the low intensity peaks at 932.6 and 952.5 eV. The peaks of higher intensities at 934.3 and 954.2 may be attributed to the gaining of an electron from the amino and carboxyl atoms during the adsorption process. A comparable shift was also reported in previous research work [22]. The N 1s species of sludge and EDTA-CS modified sludge were identified at 399.90 and



Fig. 12. (a) Desorption kinetics of adsorbent in 0.1 M HCl solution and (b) regeneration of Cu(II) adsorbed EDTA-CS modified sludge.



Fig. 13. (a) XPS survey of sewage sludge, EDTA–CS modified sludge, and EDTA–CS modified sludge-Cu(II), (b) XPS spectra of Cu(II) 4s and 4p adsorption peaks on the adsorbent, (c) N 1s, (d) O 1s and (e) C 1s spectra of sewage sludge, EDTA–CS modified sludge and after adsorption of Cu(II), respectively.

400.81 eV and assigned as -NH⁻ and -NH^{*+}. The peak of 401.81 shifted to a higher intensity at 401.73 eV (Fig. 13c), the enhancement of N 1s peak in the modified sludge was indicative of the added amine groups. After adsorption of Cu(II), the N 1s peak shifted to 399.87 eV (Fig. 13c). This represents the change in oxidation state of the N atoms on the adsorbent surface with the donation of electrons into the shared bond between N atoms and Cu(II), altering the cloud density of electrons in the reduced N atoms [48]. In the spectrum of O 1s (Fig. 13d), the unmodified sludge shows characteristic peaks at 531.66, 532.75, and 533.70, which could be assigned to C=O, C–O–H, and O–C=O bonds, respectively [50]. After surface modification, these peaks shifted toward lower intensities 531.63, 532.73, and 533.67, respectively. This may be due to the changed chemical interactions of the carboxyl functional groups. With respect to the O 1s spectra (Fig. 13d) the adsorption of Cu(II) showed the O–C=O functional group

Valence	Proposed components	Sludge		EDTA–CS modified sludge		EDTA-CS modified sludge-Cu	
		Binding energy (eV)	Relative quantity (%)	Binding energy (eV)	Relative quantity (%)	Binding energy (eV)	Relative quantity (%)
	C–C	284.79	32.20	284.83	36.86	284.82	36.37
C 1s	C–N	286.24	54.31	286.34	45.33	286.23	38.08
	O-C=O	288.08	13.49	288.03	17.80	287.90	25.56
NT 1	-NH-	399.90	84.83	399.77	77.90	399.97	87.99
IN IS	-NH*+-	400.81	15.17	401.77	22.10	401.67	12.01
	C=O	531.66	48.66	531.63	42.85	531.37	35.64
O 1s	С-О-Н	532.75	43.23	532.73	50.08	532.56	59.11
	O-C=O	533.70	8.11	533.67	7.07	533.74	5.36

Table 4Summary of binding energies and relative contents of elements

binding energy shift to 533.74 together with a decrease in the peak area ratio (Table 4) from 7.07% to 5.36%. This shift can be attributed to the Cu(II) interaction with a carboxyl group donating electrons to the Cu(II) metal, causing a decreased in the density of electrons toward oxygen atoms. These results indicate the involvement of O-C=O groups in Cu(II) adsorption [50]. The C 1s of sludge spectra (Fig. 13e) showed three peaks at 284.79, 286.24, and 288.08 eV, characteristic of C-C, C-N, and O-C=O bonds, respectively [51]. After the surface modification, the O-C=O peak area ratio (Table 4) increased from 13.49% to 17.80%, due to the additional number of carboxyl functional groups of the EDTA moiety. No significant changes were observed in the spectra of C 1s (Fig. 13e) after Cu(II) adsorption, demonstrating that the N and O atoms are the principle binding sites for the Cu(II) on the EDTA-CS modified sludge.

Cu(II) has a d9 electron shell from which an electron can be promoted to a 4p orbital, resulting in ds2p hybrid orbit formation. This hybrid orbit can accept an electron and complex with the donor of the electron. Hence the functional groups of the EDTA–CS modified sludge can provide the electron lone pair and coordinate with the Cu(II) during the adsorption process, explaining the enhanced chelating (adsorption) capacity of the EDTA–CS modified sludge.

4. Conclusion

In this study, sewage sludge was modified by surface crosslinking EDTA–CS in a simple one-pot reaction. The success of the modification was confirmed by SEM, FTIR, TGA, XRD, BET, and XPS studies. The EDTA–CS modified sludge greatly enhanced the capacity of sewage sludge to quickly and successfully adsorb Cu(II), even in the presence of other potentially competing cations, including ammonia. The maximum metal uptake by the modified sludge was 42.4 mg g⁻¹ at pH 3.0. The XPS data indicated the adsorption mechanism involved the amino, hydroxyl, and carboxyl groups donating electrons into a bond with the adsorbed Cu(II) ions. Furthermore, the adsorption was found to be monolayer chemisorption. This new sewage sludge based

adsorbent also proved to have excellent stability and was able to be recycled a number of times, albeit with a small iterative reduction in capacity for each cycle. It has great potential for economically removing Cu (II) from contaminated wastewater, and possibly other heavy metal ions as well, although this will require further study.

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