

Synthesis of QCS-Glutamate: A New Source to Remove Hg (II) Ions from Wastewater

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ABSTRACT: Here we report efficient biomass-based Hg (II) bioadsorbent. *Quercus Coccifera* Shell (QCS) was recycled and modified with glutamic acid by esterification as QCS-glutamate. After the FT-IR, SEM, and BET characterizations, related optimizations like the amount of adsorbent, initial concentration, temperature, and initial pH were studied to reach optimal adsorption efficiency. Then the adsorption and kinetic studies of the produced QCS-glutamate showed that Hg (II) was successfully adsorbed on QCS-glutamate with high adsorption maxima (q_{max}) and followed the Lagergren pseudo-second-order reaction and Langmuir adsorption isotherm model ($R^2 \geq 0.99$). The maximum adsorption capacities (q_{max}) of QCS and QCS-glutamate were found as 35.71 and 70.42 mg/g, respectively while standard enthalpy (ΔH°) standard free energy (ΔG°) and standard entropy (ΔS°) were found as 34.31 kJ/mol, 87.58 kJ/mol and -178.74 J/mol K respectively. This finding suggests that a novel bioadsorbent QCS-glutamate is a cost-effective and promising bioadsorbent for the removal of Hg (II) ions from wastewater.

KEYWORDS: Hg (II); QCS-glutamate; Langmuir isotherm; Remediation; Kinetics.

INTRODUCTION

The rapid increase of worldwide water pollution incidents caused by toxic heavy metals has been triggering a series of detrimental risks to human health and the entire global biosphere since toxic heavy metals derivative with lethal toxicity even at trace concentrations, non-biodegradability, environmental sustainability, and amplification [1, 2]. They are labeled as the prior

pollutants and the removal of heavy metals from industrial wastewater and combustion facilities have been crucial. Mercury comes forward on the list of heavy metal pollutants in aquatic environments [3, 4]. Mercury compounds are widely used in industrial plants from paint production to pharmaceuticals, from waste batteries to mining [5, 6]. The release of heavy metals to the environment without

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pretreatments and filtration causes the lethal consequences [7]. The bioaccumulation of mercury in the food materials can cause various diseases such as tyrosinemia, dyspnoea, pulmonary and kidney dysfunctions. The most sensational ecological events had been reported from the Minimata's bay in Japan during the 1950s [8]. According to the European Union, the maximum amount of the permitted total mercury discharge into drinking water is 1 µg/L while it is 5 µg/L in wastewater. Several methods have been established for the removal of Hg (II) ions, including membrane technologies, reverse osmosis, chemical pretreatment and filtration of their halide salts, coagulation, photoreduction, chromatography, featured adsorption, and electro dialysis [9]. For decades, adsorption has been preferred as a very useful heavy metal removal method for the remediation of wastewater and drinking waters [10]. Since this method is very cost-effective, bio-compatible, eco-friendly, and highly effective, is generally preferred among the other developed technologies for the removal of divergent heavy metals. The scale of the biomaterials used for this purpose has a very large spectrum such as activated carbon, nanotubes, silica and zeolites, and numerous modified carbon-based materials [11-13].

Especially, biomass-based active carbons have been extensively utilized for this purpose, due to the many advantages of bio-sourced materials such as being very cost-effective, environmentally friendly, easily recycled, carbon-free, completely late last long Sobhanardakani [14]. In some studies, the -OH terminus of the cellulose has been converted into organic acids, amidoxime, amino, sulfhydryl, and carboxylates [15] to enhance the selective heavy metal adsorption functions of this material [16, 17]. Similarly, we previously reported some original functionalization techniques for the immobilization of heavy metals including complexations and chelate compositions [18]. Apart from the reported studies, herein we firstly, report the natural and glutamic acid-modified *Quercus coccifera* shell (QCS) which is a very abundant biomass present in the Mediterranean region [19], as a bioadsorbent to increase the adsorption capacity of Hg (II) ions in aquatic media. The chemical characterizations of the QCS and the glutamic acid-modified QCS (QCS-glutamate) were performed by FT-IR, SEM, and BET. After that, a series of optimizations belong to Hg (II) ion removals such as the time, pH, and initial Hg (II)

concentrations, adsorption temperature and the adsorbent dosage. Finally, the adsorption kinetics and isotherms were examined in detail for each.

EXPERIMENTAL SECTION

Reagents

All the chemicals were of analytical grade, HNO₃, HCl, HgCl₂, and NaOH were purchased from Merck Corporation. All polypropylene flasks and glassware were maintained in 10 % (v/v) aqueous HNO₃ overnight and rinsed by using ultrapure water several times. Hg (II) solution was used without adjusting pH otherwise needed.

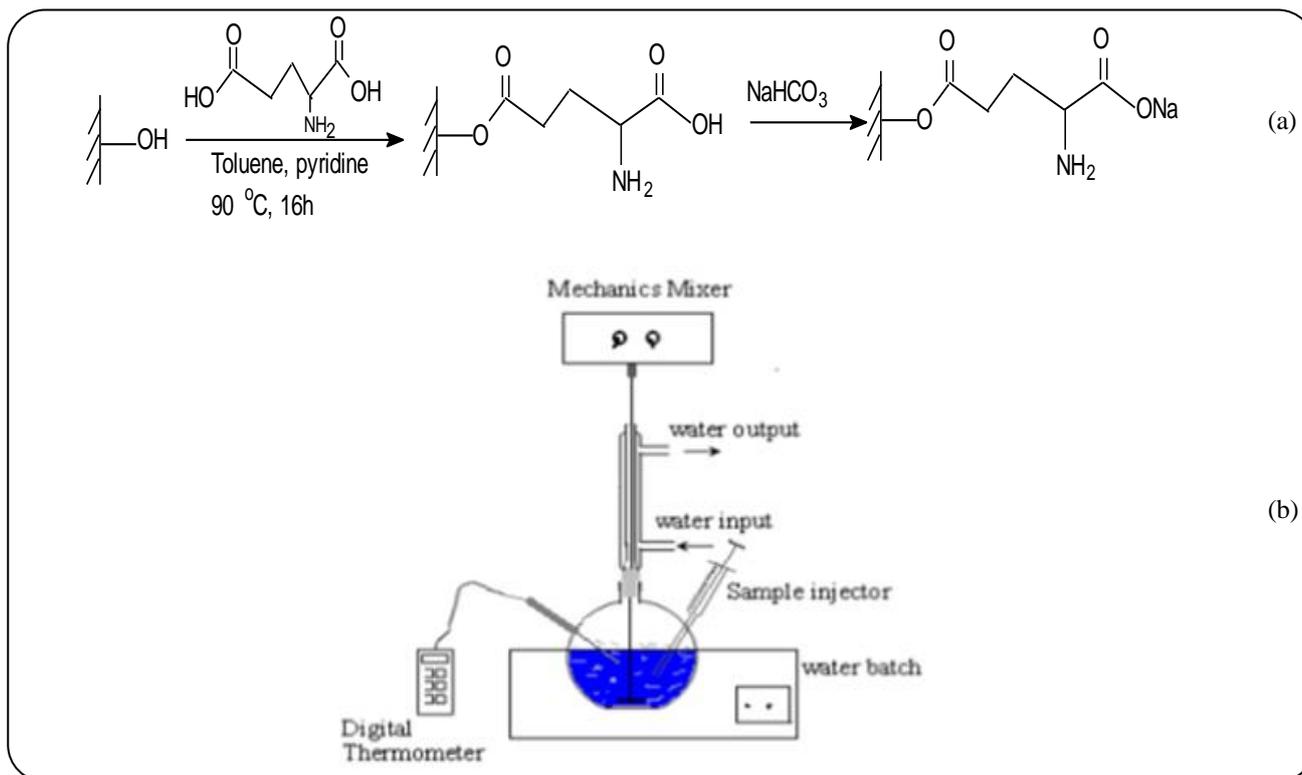
Equipment

WTW 330 i pH meter was used for the pH adjustments. Zhwy-200D brand mechanical shaker, GBC atomic absorption spectrometer equipped with slotted Tube Atom Trap (STAT), deuterium lamp background corrector and air/acetylene flame were used in the adsorption studies. SEM with EDS monitored with JEOL, JSM-7600F. FT-IR measurements were performed with a Perkin Elmer-ATR-supported FT-IR analyzer. BET measurements were recorded with Quantachrome Surface Area and pore analyzer NOVA 2200e.

Preparation of QCS-Glutamate and adsorption studies

Samples of QCS were collected from the Muğla region of Turkey. The shells were cleaned using deionized water to remove surface particles. 5 g of QCS biomass was smoothly crushed and transferred to a mixture of 34 mL 30% formalin and 66 mL 0.1 mol/L HCl solution to increase surface area. QCS was modified with glutamate and derivatized in toluene (400 mL) and pyridine (60 mL) using the glutamic acid (6 g) at 60 °C, and stirred overnight at 90 °C. The resulting crude QCS-glutamate was cooled down to 60 °C then filtered and washed with acetone. After drying the QCS-glutamate yielded product was obtained as 33.5 g. The obtained powder was sieved through 0.5 mm mechanical sieve.

QCS-glutamate, the modified bioadsorbent, was neutralized by treating with concentrated NaHCO₃ solution (Scheme 1a). After that, the obtained product was filtered and rinsed with distilled water and then acetone to remove excess glutamate. Then, it was dried under a vacuum and sieved through a 0.5 mm manual sieve. The optimum adsorption conditions were examined



Scheme 1: Synthesis of glutamate-QCS (a) and Adsorption experiment setup (b).

for contact time (0-150 min), pH (3-9), Hg (II) concentration (25-100 mg/L), temperature (25-45) and bioadsorbent dosage (0.5-2 g/L) for the developed bioadsorbent. The adsorption process was performed by mixing the Hg (II) contaminated solution and QCS-glutamate in erlenmeyer flasks by shaker system in a water bath at 180 rpm. The treated mixture was filtered. The filtrates were subjected to atomic absorption spectrometer to measure the amount of Hg (II) adsorbed on the surface of the bioadsorbent. Measurement sensitivity was increased by using STAT [19]. All the experiments were duplicated (Scheme 1b).

RESULTS AND DISCUSSIONS

This study aimed to prepare a bioadsorbent that would be cheap, easy to prepare and handle and would cause no risk to environment. For this purpose, we desired to prepare a bioadsorbent from QCS and glutamic acid, characterized and studied against various factors. The following extended measurements were carried out to reach the knowledge that the prepared QCS-glutamate can remove Hg (II) from aqueous solutions successfully.

Biadsorbent characterization

FT-IR results of QCS, and QCS-glutamate showed similar spectra but some identical differences after the glutamate modification (Fig. 1a, b). The spectrum given in Fig. 1b belongs to QCS-glutamate, and shows a broad stretching band at 3100-3600 cm^{-1} that can be related to $-\text{NH}$ and/or $-\text{OH}$ stretching vibrations. Another bending vibration band at 1035.72 cm^{-1} is also present in the spectrum that can be C-O and C-N stretchings. It means that both amine and hydroxyl are present in the product that corresponds to QCS-glutamate. Other important stretching bands at 2926.90 and 1512.80 cm^{-1} are attributed to C-H CH_2 group of cellulose and hemicellulose [20] and N-H, respectively [21].

SEM has been globally utilized to analyze surface morphology and its characteristics. Fig. 2 (a, b) shows the SEM images of QCS and QCS-glutamate surfaces. It can be clearly seen that the surface of QCS is heterogeneous and porous. After the QCS particles were covered by glutamate molecules the cavities were filled and morphology showed significant changes. As a result of glutamate modification, it can be concluded that the surface area was increased as reported earlier [18].

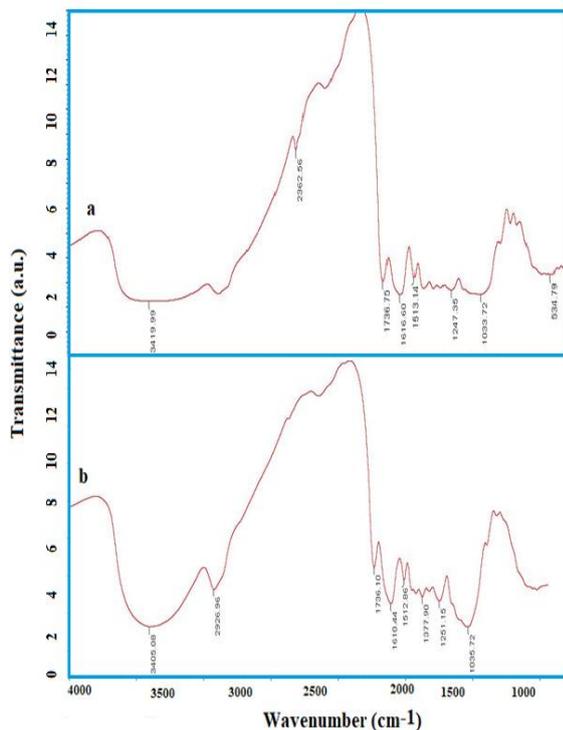


Fig. 1: FT-IR spectra of (a) raw QCS and (b) QCS-glutamate.

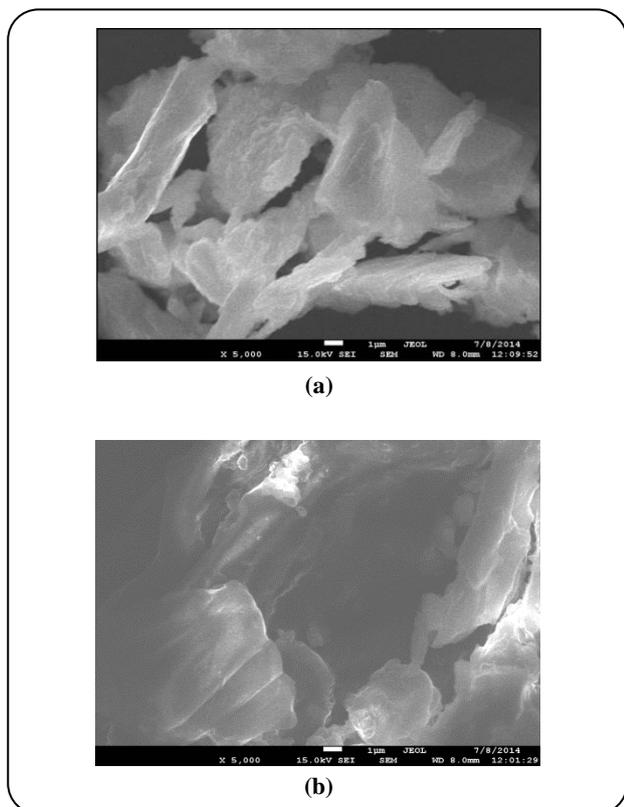


Fig. 2: SEM images of (a) raw QCS; (b) QCS-glutamate.

The increase of the surface area of QCS was also verified with BET analysis before and after the modification with glutamate. The unmodified form of the QCS showed a surface area of $108.53 \text{ m}^2/\text{g}$ whereas the surface area of QCS-glutamate was increased to $129.64 \text{ m}^2/\text{g}$ due to the modification. Therefore, it is proved that the glutamate molecules increased the active surface area of the QCS, thus the adsorption capability of the material was enhanced. The results were the achievements of *Kanwal et al.*, they reported similar enhancements results on the Cr (III) adsorption study onto polyaniline/rice husk adsorbent [22].

pH effect

pH can affect the ionization of functional groups of the adsorbent that changes the charge properties of the adhered surface [23]. Fig. 3 shows the effect of pH (3-9) on the Hg (II) adsorption on the prepared bioadsorbent. The Hg (II) uptake capacity of QCS-glutamate increased by increasing pH values from 3.0 to 7.0 and stayed steady for further values such as pH 9. The equilibration was achieved around 5 to 10 min. for every pH value then the results reached a plateau of up to 150 min. of adsorption. At the lower pH values, the protons (H^+) and Hg (II) ions are challenged to capture the active sites of QCS-glutamate. Since the number of competing protons decreases due to the pH increment, the adsorption of the Hg (II) ions is enhanced. At the higher pH values the Hg (II) ions were desorbed because of the dissociation of the amine and carboxylate groups that were located on the surface of QCS-glutamate [24]. However, Hg (II) ions are not stable beyond 5.6 pH and precipitate out in the form of $\text{Hg}(\text{OH})_2$. So, the optimum pH is determined as 5.6.

The effect of initial concentration

Hg (II) uptake by QCS-glutamate bioadsorbent was investigated at various concentrations in the range of 25-100 mg/L without any external change in pH at 25°C . Fig. 4 shows that the adsorption of Hg (II) ion (mg/g) increases proportionally with the changing initial concentrations. The optimum adsorption concentration was found as 42.30 mg/g which is a notable amount. This result is attributed to the amine and carboxyl group abundant nature of the biomaterials so, the complex formation with Hg (II) ions is increased while adsorption is in progress [25].

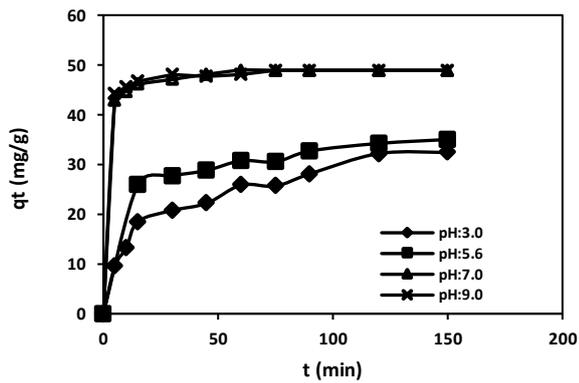


Fig. 3: Effect of pH on adsorption Hg (II) onto QCS-glutamate (mercury concentration: 50 mg/L; adsorbent dosage: 1.0 g/L; temperature: 298 K; time:150 min.)

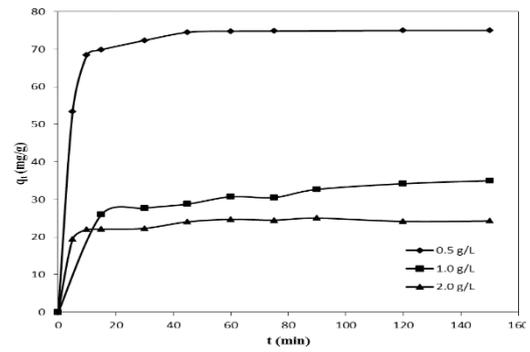


Fig. 5: The effect of adsorbent dosage on the Hg(II) ion adsorption by QCS-glutamate (Hg(II) ion: 50 mg/L; pH: 5.6; temperature: 298 K; contact time: 150 min).

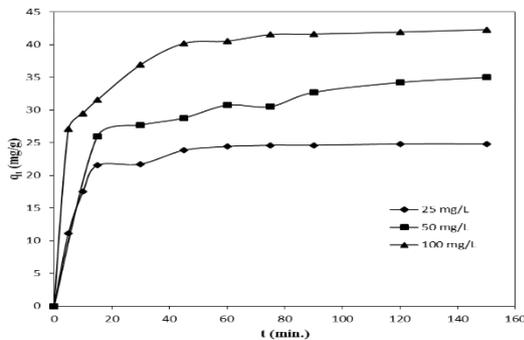


Fig. 4: Influence of initial concentration on mercury adsorption by QCS-glutamate (adsorbent dosage: 1.0 g/L; pH:5.6; temperature: 298 K; contact time: 150 min)

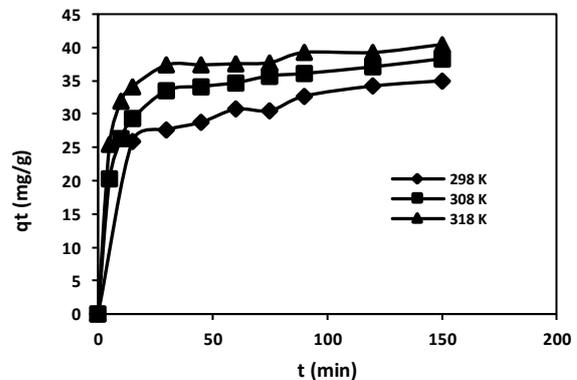


Fig. 6: The effect of temperature on the Hg (II) ion adsorption by QCS-glutamate (Hg(II) ion: 50 mg/L; adsorbent dosage: 1.0 g/L; pH: 5.6; contact time: 150 min)

The effect of adsorbent dosage

The QCS-glutamate bio-adsorbent dose was studied against the removal of Hg (II) as shown in Fig. 5. The adsorption dosage of Hg (II) increased from 0.5 to 2.0 g/L by changing the adsorption capacity per unit weight of QCS-glutamate from 75.00 to 24.28 mg/g. These results point that the adsorbent dosage is inversely proportional to the amount of adsorption. It is well known that the amount of the adsorbed material will be increased when there are more active sites available [26].

The effect of temperature

The Hg (II) adsorption capacity of the QCS-glutamate was increased by the temperature increase (Fig. 6). 35 mg/g of Hg (II) was adsorbed on the bioadsorbent

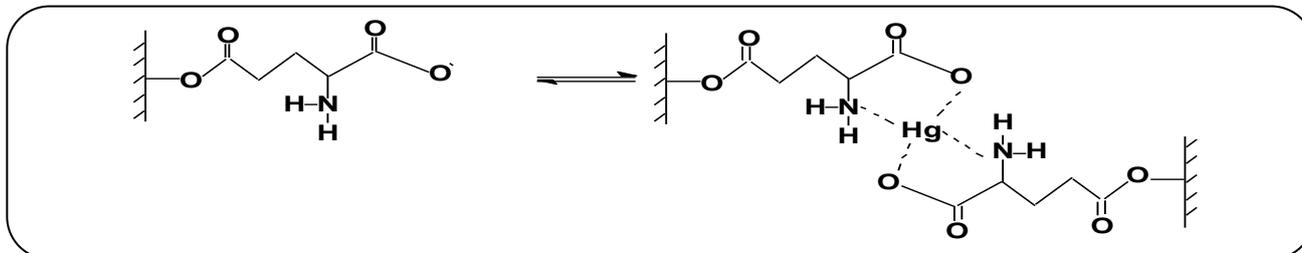
at 298 K (contact time: 2.5 h). This amount was increased to 40.44 mg/g when the temperature of the reaction mixture was increased to 318 K. It means that the adsorption process of the presented system is endothermic. Similarly, *Dindar et al.* reported in their previous report on the adsorption of Hg (II) on the activated carbon obtained from the palm shells, that a higher temperature is more favorable to adsorbing Hg (II) ions [27].

Sorption mechanism

QCS-glutamate is rich in various active functional groups that coordinate with metals. Therefore, the carboxyls (-COOH) and amines (-NH₂) ligands, which are present on the surface of QCS-glutamate, do supramolecular interactions with mercury (II) ions

Table 1: The characteristic isotherm parameters of the adsorption process of Hg (II) on QCS and QCS-glutamate.

Adsorbents	Langmuir isotherm				Freundlich isotherm
	q_m (mg/g)	K (L/mg) $\times 10^2$	R^2	R_L	R^2
QCS	35.71	3.28	0.98	0.19-0.86	0.85
QCS-glutamate	70.42	6.79	0.99	0.09-0.44	0.74

**Scheme 2: A plausible mechanism for the adsorption of Hg²⁺ ions on QCS-glutamate.**

as reported previously [25, 28]. The complex formation of Hg (II) with the ligands of QCS-glutamate is shown in Scheme 2.

Adsorption isotherms

In this study, Hg (II) adsorption onto QCS-glutamate (1.0 g/L) was analyzed at different concentrations of 5-200 mg/L at the optimal pH and temperature. The interaction between adsorbate and adsorbent can be easily correlated by plotting Langmuir and Freundlich's adsorption isotherms. It is well known that monolayer adsorption isotherm is represented by the Langmuir model where the surface is homogeneous; all active sites are of the same energy. In contrast, the Freundlich adsorption model is used where the surface is heterogeneous; adsorption sites are of different energies, and multilayer adsorption occurs [29, 30]. The correlation coefficients and adsorption constants were calculated by using the isotherms (Table 1).

Equation 1 shows the calculation of q_e which is the equilibrium adsorbate concentration on the adsorbent surface (mg/g).

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

where q_m is the maximum amount of adsorption (mg/g). K represents the affinity constant (L/mg), and C_e is the solution concentration at equilibrium (mg/g). The straight-line equation of Langmuir adsorption isotherm is provided in Eq. (2) as follows:

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

Slope and intercept can be obtained after the calculations from the plot of C_e/q_e versus C_e/q_m and K [20]. The Freundlich adsorption isotherm can be represented by the formulae given in Eqs. (3) and (4):

$$q_e = K_F C_e^n \quad (3)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (4)$$

Where C_e is the concentration of solution at equilibrium and q_e is the amount of adsorbate adsorbed per unit weight of adsorbent. In the Freundlich equation, the constant K_F represents the adsorption capacity while n shows the intensity [18, 20].

The equilibrium adsorption behavior of this study agrees with the Langmuir model (Table 1). QCS and QCS-glutamate maximum adsorption capacity (q_m) determined by this model were found as 35.71 and 70.42 mg/g, respectively.

The Langmuir adsorption isotherm can be expressed by a constant R_L "a dimensionless separation/equilibrium parameter" [30]. Equation 5 shows the calculation of R_L .

$$R_L = \frac{1}{1 + K C_e} \quad (5)$$

The R_L values were calculated and are provided in Table 1. R_L constant was found between 0 and 1. It means

Table 2: The kinetic parameters obtained by the presented study.

Kinetic models								
T(°C)	[C ₀] (mg/L)	pH	Adsorbent dosage (g/L)	Pseudo- first order R ²	Pseudo-second order			
					q _{e(cal.)} (mg/g)	q _{e(exp)} (mg/g)	k ₂ × 10 ⁻³ (g/mg.min)	R ²
25	50	5.6	1.0	0.916	35.00	35.30	2.734	0.99
35	50	5.6	1.0	0.929	38.30	38.90	4.535	0.99
45	50	5.6	1.0	0.841	40.44	40.45	6.968	0.99
25	50	3.0	1.0	0.792	32.38	32.96	1.893	0.99
25	50	7.0	1.0	0.978	48.91	49.26	21.352	0.99
25	50	9.0	1.0	0.723	48.91	49.26	21.352	0.99
25	25	5.6	1.0	0.950	24.80	25.08	9.275	0.99
25	100	5.6	1.0	0.957	42.30	42.66	5.360	0.99
25	50	5.6	0.5	0.971	75.00	75.05	10.505	0.99
25	50	5.6	2.0	0.798	24.28	24.69	32.808	0.99

that the adsorption is favorable for Hg (II) and occurs on the bioadsorbent surface.

Kinetics analysis

The atomic absorption technique was used to follow the adsorption progress. The data shows the decrease in the amount of Hg (II) the time passed (0-150 min). The obtained data were plotted for both pseudo-first order and pseudo-second-order kinetics. The pseudo-first-order kinetic model was proposed by Lagergren for the adsorption of solid/liquid systems that can be expressed in the form of a formula given in Eq. (6) [31, 32].

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (6)$$

where q_e and q_t (mg/g) are the amount of adsorbate adsorbed on the surface of the adsorbent at equilibrium and at time t (min), respectively. The k_1 (min⁻¹) shows that the sorption rate constant is of first order. Linear plots of $\log(q_e - q_t)$ versus t indicate the usability and applicability of this kinetic model. R² values were calculated from the slopes (Table 2) [33]. The pseudo-second-order kinetic model [34] is expressed in Eq. (7).

$$\frac{t}{q_t} = \left[\frac{1}{k_2 q_e^2} \right] + \frac{t}{q_e} \quad (7)$$

Where k_2 and q_e are the adsorption rate constant (g/mg min) and the amount of adsorbate (mg/g) at equilibrium,

respectively. The slope was calculated from the values of t/q_t versus t and is shown in Table 2. The results were plotted for pseudo-first order and pseudo-second order. A pseudo-second-order kinetic model was found as the best fit for the adsorption.

Comparison with other adsorbents

The data collected from the literature with the q_{max} values are provided in Table 3 and compared with prepared QCS and QCS-glutamate bioadsorbent. *Inbaraj et al.* [35] studied the adsorption of mercury ions on the extracellular biopolymer poly(c-glutamic acid) and found 96.79 mg/g maximum adsorption. In this study, we found the highest adsorption on the QCS-glutamate at 70.42 mg/g. There are other reports on the adsorption of Hg(II) on various active adsorbents but the q_{max} found is less than we obtained. *Wang et al.* [36] adsorbed Hg (II) on 4-aminoantipyrine and also obtained notable results (q_{max} : 52.90 mg/g). Other adsorbents used to adsorb Hg (II) are SBA/NH₂ [27], biomatrix from rice husk [37], wool-g-PIAH [38], etc. but the maximum adsorption capacity obtained was lower.

Adsorption thermodynamic

Arrhenius equation (Eq. (8)) was used to calculate the activation energy E_a of adsorption [6].

$$\ln k_2 = \ln k_0 - \frac{E_a}{R_g T} \quad (8)$$

Table 3: Evaluation of the maximum adsorption of Hg (II) in this study versus different adsorbents.

Adsorbents	q _{max} . (mg/g)	References
SBA/NH ₂	7.59	[27]
4-aminoantipyrine immobilized bentonite	52.90	[36]
Biomatrix from rice husk	36.10	[37]
Wool-g-PIAH	49.33	[38]
SG-HO-S-AO	0.57	[39]
N-methylacrylamide-co-acrylic acid	11.00	[40]
Raw QCS	35.71	Presented study
QCS-glutamate	70.42	Presented study

In Eq. (8), k_0 is the frequency factor. The activation energy (E_a) was calculated from the slope of the linear plot of $\ln k_2$ versus $1/T$. Adsorption can be chemical or physical. Generally, the E_a of chemisorption lays between 65 and 250 kJ/mol. During this study, the activation energy to adsorb Hg(II) onto QCS-glutamate surface was found as 36.87 kJ/mol. It means that the Hg(II) physically adsorbed (physisorption) on the surface of QCS-glutamate [41].

Gibbs free energy (ΔG°), enthalpy of adsorption (ΔH°), and entropy (ΔS°) can be used to know the nature and mechanism of the adsorption process. These parameters were determined from the Eyring formula given in Eq. (9) [18, 20].

$$\ln\left(\frac{k}{T}\right) = \ln\left(\frac{k_b}{h}\right) + \frac{\Delta S^\circ}{R_g} - \frac{\Delta H^\circ}{R_g T} \quad (9)$$

In Eq. (9), h is the Planck's while k_b is Boltzmann's constants. According to Eq. (9) $\ln(k/T)=y$; $1/T=x$; $-(\Delta H^\circ/R_g)=m$ and $[\ln(k_b/h)+(\Delta S^\circ/R_g)]=n$ in the linear equation of $y=mx+n$. ΔH° and ΔS° values can be calculated as the m and n values of this equation. The Gibbs free energy (ΔG°) values were obtained by using Eq. (10).

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad (10)$$

ΔG° was determined at 298 K from Eq. (10). ΔG° , ΔH° , and ΔS° of activation were found as 87.58 kJ/mol, 34.31 kJ/mol, and -178.54 J/mol K, respectively. ΔH° found was found positive which means the reaction was endothermic [42].

CONCLUSION

The QCS-glutamate-modified bioadsorbent was synthesized and characterized using various techniques. The adsorption capacity of QCS-glutamate to remove Hg (II)

was enhanced significantly when compared to the QCS. Adsorption of Hg (II) on the QCS-glutamate surface followed a pseudo-second order kinetic model. The maximum adsorption capacities (q_{max}) of QCS and QCS-glutamate were found as 35.71 and 70.42 mg/g respectively, while standard enthalpy (ΔH°), standard free energy (ΔG°), and standard entropy (ΔS°) were found as 34.31 kJ/mol, 87.58 kJ/mol, and -178.74 J/mol.K respectively. The data obtained was applied to Langmuir and Freundlich's adsorption isotherm models. Langmuir isotherm model was found as most suitable. Although the presented biomass-based method shows some shortages such as the long-term stability, but it can be improved in various ways. In this study, the removal of the heavy metal Hg (II), which is very important, was successfully achieved, and it is predicted that the QCS-glutamate bioadsorbent has a high removal potential for the Cr (III), Mn (II), Fe(III), Ni(II), Cu(II), Zn(II), and Pb(II) ions and a great candidate for successful removal of these ions in future studies.

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