Modelling and Optimising the Performance of Graphene Oxide-Cu2SnS3-Polyaniline nanocomposite as an Adsorbent for Mercury Ion Removal

Modelling and Optimising the Performance of Graphene Oxide-Cu_2SnS_3-Polyaniline nanocomposite as an Adsorbent for Mercury Ion Removal

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Abstract

Finding a cost-effective, efficient and environmentally friendly technique for removal of mercury ion (Hg^{2+}) in water and wastewater can be a challenge task. This paper presents a novel and efficient adsorbent known as the Graphene oxide-Cu_2SnS_3-Polyaniline (GO-CTS-PANI) nanocomposite, which was synthesised and utilised to eliminate mercury ions (Hg^{2+}) from water samples. The soft–soft interaction between Hg^{2+} and sulfur atoms besides chelating interaction between -N and Hg^{2+} and also electrostatic interaction are the main mechanisms for Hg^{2+} adsorption onto the GO-CTS-PANI adsorbent. Various characterisation techniques, including Fourier transform infrared spectrophotometry (FT-IR), Field Emission Scanning Electron Microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDX), Elemental Mapping analysis, and X-ray diffraction analysis (XRD), were employed to analyse the adsorbent. The Box-Behnken method, utilising Design Expert Version 7.0.0, was employed to optimise the crucial factors influencing the adsorption process, such as pH, adsorbent quantity, and contact time. The results indicated that the most efficient adsorption occurred at pH 6.5, with 12 mg of GO-CTS-PANI adsorbent, and a 30-minute contact time, achieving a maximum removal rate of 95% for 50 mg/L Hg^{2+} ions. The study also explored the isotherm and kinetics of the adsorption process, revealing that adsorption took place in sequential layers (Freundlich isotherm) and was followed by a physical interaction between the adsorbent and the adsorbate. The pseudo second-order kinetic equation proved to be a suitable model for interpreting the kinetic data. Furthermore, Response Surface Methodology (RSM) analysis indicated that pH was the most influential parameter in enhancing adsorption efficiency. In addition to traditional models, this study employed artificial intelligence methods, such as the Random Forest algorithm, to enhance the prediction of adsorption process efficiency. The findings demonstrated that the Random Forest algorithm exhibited high accuracy, achieving a correlation coefficient of 0.98. Overall, this research underscores the potential of the GO-CTS-PANI composite for effectively removing Hg^{2+} ions from water resources.

Keywords: *Adsorption, Artificial Intelligence, Graphene oxide-Cu_2SnS_3-PANI, Mercury ion, Response Surface Methodology*

Introduction

In the present era, addressing heavy metal pollution poses a significant challenge to environmental preservation (Briffa et al., 2020). One such hazardous metal is mercury ion (Hg^{2+}), which exhibits toxicity even at low concentrations, leading to detrimental impacts on various bodily systems, including the nervous, digestive, immune, respiratory, and renal systems (Raj and Maiti 2019; Rice et al., 2014). The presence of Hg^{2+} in the environment is primarily attributed to human activities such as gold mining, alloy manufacturing, smelting, electricity and pesticide production, paint manufacturing, and waste incineration (Tchounwou et al., 2003; Mbanga et al., 2019; Streets et al., 2011). It infiltrates water resources through processes like atmospheric deposition, surface runoff, and direct discharge from industries and sewage treatment facilities. Once in water, Hg^{2+} can be converted into methylmercury by bacteria, a highly toxic form of the element. Methylmercury accumulates in the food chain, particularly in aquatic organisms like fish, resulting in biomagnification and posing a health risk to humans when consumed (Global Mercury Assessment 2018; Yu et al., 2016). According to the recent Global Mercury Assessment, approximately 2000-2500 tonnes of mercury are released into the atmosphere, water, and soil each year (Global Mercury Assessment 2018). Consequently, the removal of Hg^{2+} from environmental water samples is of paramount importance.

Various techniques, including adsorption (Yu et al., 2016; Santana et al., 2016), membrane filtration (Albatrni et al., 2021; Yan et al., 2021), ion exchange (Han et al., 2020), and coagulation (Vasudevan et al., 2012), have been employed for this purpose. Among these, adsorption is the most commonly used method due to its inherent advantages, including the ease of preparing synthetic and natural adsorbents, relatively low cost, and high removal efficiency (Saadati et al., 2023; Rezazadeh et al., 2022; Wei et al., 2018; Li et al., 2014; Lei et al., 2014).

Graphene oxide (GO) is an oxidised form of graphene featuring oxygen-based functional groups that render it hydrophilic and readily dispersible in aqueous solutions. Its surface can be chemically or physically modified with various functional groups, making it suitable for a range of applications, including water treatment (Arshad et al., 2019; Amini-Fazl et al., 2021). Ternary Cu_2SnS_3 (CTS) is an environmentally friendly material with optoelectronic properties, well-suited for photoelectrochemical applications (Jathar et al., 2021). It also contains readily available elements, making it a cost-effective material (Berg et al., 2012). Furthermore, the presence of sulfur atoms (soft base) in CTS makes it an effective adsorbent for toxic soft heavy metals like Hg^{2+} (Velempini and Pillay 2019). Thus, the main purpose of the proposed method is to synthesise and characterise of GO-CTS-PANI nanocomposite to be used as an adsorbent that would maximise the efficiency of the removal of Hg^{2+} ions from water sample. This can be achieved by synthesising CTS nanoplates and then its characterisation to modify GO followed by modification with PANI. Since CTS nanoplates have Sulphur atoms in its structure, it could be served as a suitable adsorbent for the removal of Hg^{2+} as a very toxic ion. Hence, this study first aims to synthesise GO nanosheets using the Hummer method and modify them with CTS nanoplates and polyaniline (PANI) to create the GO-CTS-PANI nanocomposite. The synthesised adsorbent undergoes thorough characterisation using various techniques, including Fourier transform infrared spectrophotometry (FT-IR), Field Emission Scanning Electron Microscopy (FESEM), Energy-dispersive X-ray spectroscopy (EDX), Elemental Mapping analysis, and X-ray diffraction analysis (XRD). To determine the optimal conditions for achieving the maximum removal percentage (RP), the Box-Behnken experimental design is employed, and various isotherm and kinetic models are assessed and interpreted. Finally, both the Box-Behnken method and Random Forest algorithms are utilised for optimising and predicting the performance of the adsorption system, respectively.

Methodology

This study is divided to different parts including experimental and numerical efforts which are demonstrated in **Figure 1**. According to the scheme, it can be found that experimental practices containing the characterisations and adsorption application process. Likewise, the numerical parts including classical computations for adsorption mechanism analysis, optimisation by Response Surface Methodology, and Machine Learning calculations.

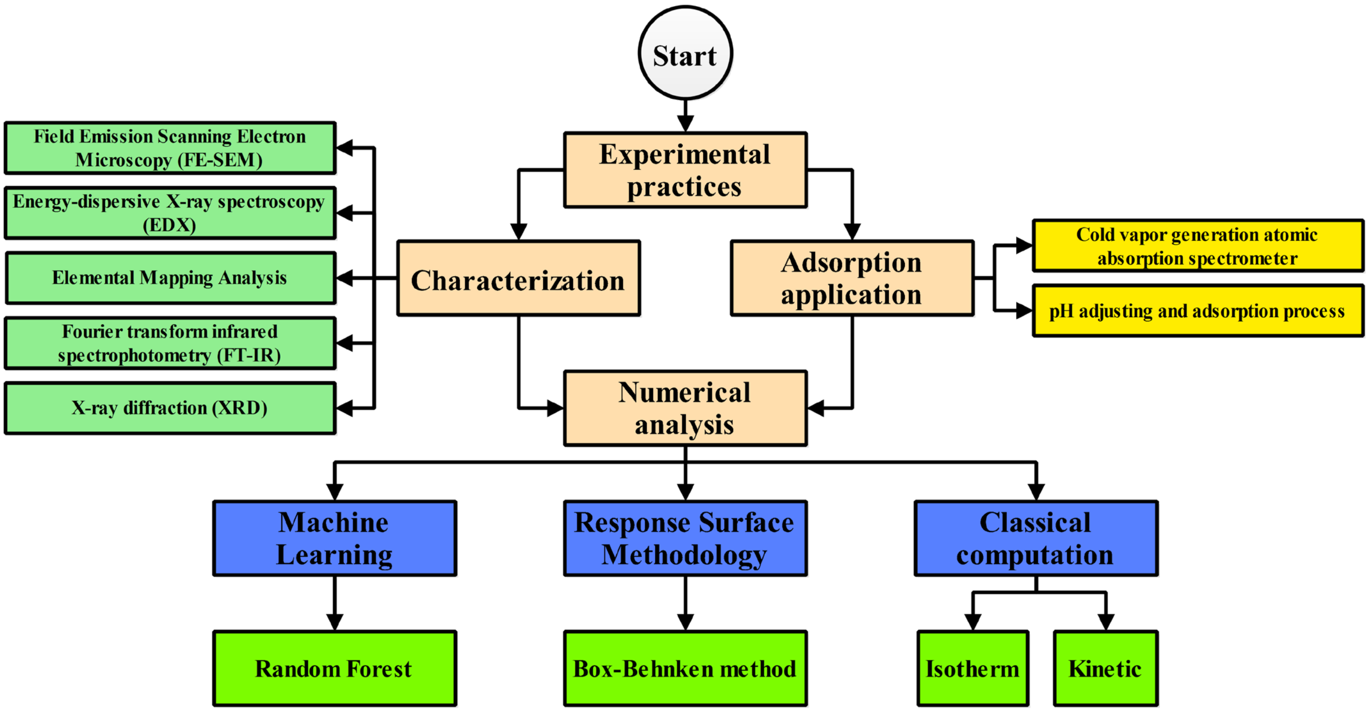


Figure 1. The research roadmap of this study.

Instruments

FE-SEM, EDX, and Elemental Mapping Analysis were conducted using a BRNO-Mira3 LMU device manufactured by TESCAN in the Czech Republic. FT-IR analysis was performed with an AVATAR 370 spectrometer from the US, and XRD analysis utilized a D8-Advance Bruker Cu Kα1 instrument, also from the US. To determine the concentration of Hg^{2+}, a cold vapor generation atomic absorption spectrometer (CV-AAS, Perkin Elmer Analyst 700, USA) equipped with a Hg hollow cathode lamp emitting at 253.7 nm was employed. pH adjustments were made with a Metrohm 827 pH-meter from Switzerland, and the separation of the adsorbent from the solution was accomplished using an Andreas Hettich D72 centrifuge instrument from Germany.

Reagents

The following reagents and chemicals were used in the experiment: Mercury nitrate monohydrate (Merck, Germany) to prepare a 1000 mg L^{-1} Hg^{2+} solution, Graphite, $Cu(NO_3)_2.3H_2O$, $SnCl_2.2H_2O$, thiourea, aniline, ammonium persulfate, H_2SO_4 (98.0%), $KMnO_4$ (99.0%), H_2O_2 (30%), sodium borohydride ($NaBH_4$, 99.0%) and HNO_3 (65.0%). All of these chemicals and reagents were also provided by Merck (Germany).

Synthesis of GO-CTS-PANI nano-composite

Synthesis of GO and CTS nanoplates

GO was synthesised using the Hummers method as described in **Figure 2** (Rezazadeh et al., 2022b). On the other hand, CTS was synthesised according to the following procedure: 0.241 g $Cu(NO_3)_2.3H_2O$ and 0.114 g $SnCl_2.2H_2O$ were dissolved in 50 ml deionised water. Then 0.114 g thiourea was added to the mixture which causes to the formation of milky mixture. It was then stirred for 30 minutes and autoclaved at 180°C for 8 hours in a 100 mL Teflon-lined stainless-steel autoclave. The resulting CTS nanoplates washed with deionised water three times and dried overnight at 70 °C (Wang et al., 2017).

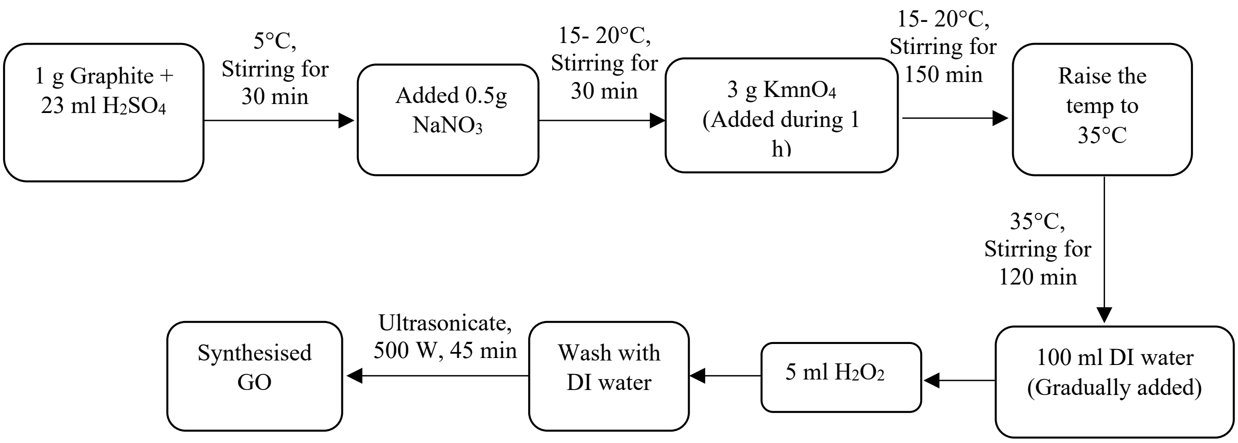


Figure 2. Synthetic route of GO in this study

Synthesise of GO-CTS nanocomposite

To prepare the GO-CTS nanocomposite; 0.5 g of the synthesised GO in 100 ml deionised water (mixture 1) and 0.15g of CTS nanoplates in 50ml deionised water (mixture 2) were separately ultrasonicated for 45 minutes to obtain uniform mixtures. By addition of mixture 2 into the mixture 1, it was stirred for 6 hours at 400 rpm. The synthesised GO-CTS nanocomposite washed with deionised water three times and dried at 60 °C overnight.

Synthesise of GO-CTS-PANI nanocomposite

In a solution containing 0.5 g of GO-CTS in 100 ml deionised water, 500 µL of aniline (in its monomeric form) was introduced and stirred for a duration of 10 minutes. Following this, 10 mL of a 1% ammonium persulfate solution was gradually incorporated into the mixture and stirred for a total of 10 h at 400 rpm. The resulting composite, known as GO-CTS-PANI nanocomposite, underwent multiple washes with deionized water and was subsequently dried overnight at 60 °C.

Removal procedure

In a test solution with an initial Hg^{2+} concentration of 50 mg L^{-1} at a pH of 6.5, 15 mg of GO-CTS-PANI was introduced, and the blend was agitated for a duration of 45 minutes. Subsequent to centrifugation for 5 min at 5000 rpm, the final concentration of Hg^{2+} at equilibrium was determined using CV-AAS. The removal percentage (RP) and the adsorption capacity (qe) were computed utilizing Equation (1) and (2), respectively.

$$RP = \frac{(C_0 - C_e)}{C_O} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_e and C_0 = equilibrium and initial concentration of Hg^{2+} in mg per litre, respectively. V= Sample volume in Lit, m= Adsorbent dosage in grams.

Optimisation process

In order to enhance the efficiency of the experiment, a Box-Behnken design was utilized through Design Expert Version 7.0.0. The Box-Behnken design belongs to response surface methodology, which constructs a second-order polynomial equation to depict the connection between the influencing factors and the response variable. These influencing factors, encompassing pH, the quantity of adsorbent (M), and contact duration, were modified across three levels, resulting in a total of 15 experimental trials. The mathematical model derived from the Box-Behnken design is represented by Equation 3, as detailed in the work of Eftekhari et al. (2020).

$$Y = \beta 0 + \beta 1X1 + \beta 2X2 + \beta 3X3 + \beta 11X1^2 + \beta 22X2^2 + \beta 33X3^2 + \beta 12X1X2 + \beta 13X1X3 + \beta 23X2X3 \quad (3)$$

Herein, Y represents the response variable, β0 is the constant coefficient, β1-β3 are the linear coefficients and β11, β22, and β33 are the quadratic coefficients. Moreover, β12, β13, and β23 are the interaction coefficients.

In the optimisation process, the model performance is examined by desirability functions based on the most important features. The function involves transforming multiple response variables into a single scalar value between 0 and 1, where a value of 1 indicates the optimal condition for all response variables, and a value of 0 indicates the worst condition. The desirability function can be described as the result of multiplying individual desirability functions, with each individual function signifying the degree of desirability for a specific response variable. The allocation of weights for these functions is determined by considering the relative significance of each response variable in relation to the overall performance of the system, as outlined in the work by Eftekhari et al. (2020).

Classical computations

The two-parameter isothermal equations represent mathematical formulas used to describe how adsorption capacity behaves under constant temperature conditions. Meanwhile, the three-parameter isothermal equations share similarities with the two-parameter equations but introduce an additional parameter to better capture the characteristics of the adsorption process (Eftekhari et al., 2020). Initially, the data is analysed using the two-parameter isotherm equations. If both the Langmuir and Freundlich models demonstrate similar performance, then the three-parameter equations are employed to precisely predict the adsorption mechanism (Eftekhari et al., 2020). In this research, both two-parameter models (Dubinin-Radushkevich, Temkin, Langmuir, and Freundlich) and three-parameter models (Toth, Khan, and Sips) are utilized to assess the adsorption mechanism. Furthermore, to evaluate the dynamic behavior of the adsorption process, several kinetic equations are applied (Eftekhari et al., 2020).

Machine Learning calculations

In this current research, the Random Forest (RF) algorithm was employed to predict the removal percentage based on various influential factors, including pH, the quantity of adsorbent, and contact time. The RF algorithm is a machine learning technique that creates numerous decision trees during the training phase and outputs either the mode of the classes (for classification tasks) or the mean prediction (for regression tasks) from the individual trees. In this specific study, the RF algorithm was trained using a dataset comprising known removal percentages and their corresponding influential factors. Additionally, to ensure the accuracy and robustness of the model, the optimal K-fold value was fine-tuned (Eftekhari et al., 2021). The K-fold technique is a method for validating a model, involving the division of the dataset into K equally sized subsets or folds. The model is trained on K-1 folds and tested on the remaining fold, with this process repeated K times. The model's performance is then averaged across the K folds to provide an estimate of its accuracy. In this study, the optimal K value was determined by adjusting the parameter through a grid search approach (Eftekhari et al., 2021). The mathematical representation of the RF algorithm can be found in Equation 4.

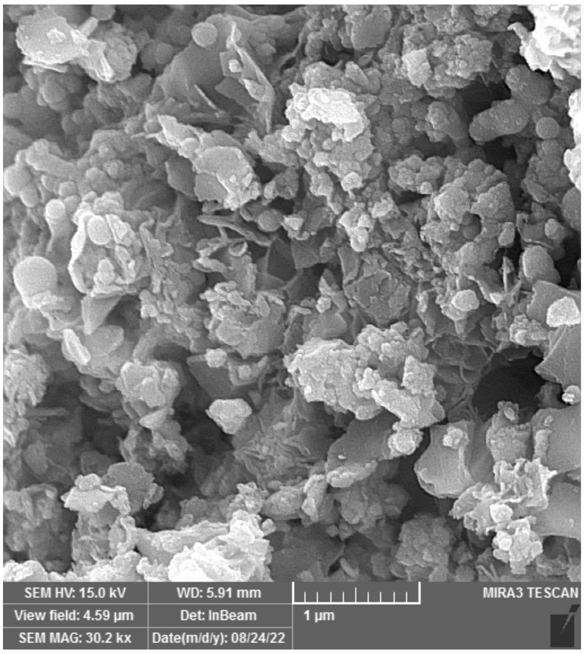
Given a training set T = {(x1,y1), (x2,y2),..., (xn,yn)} (4)

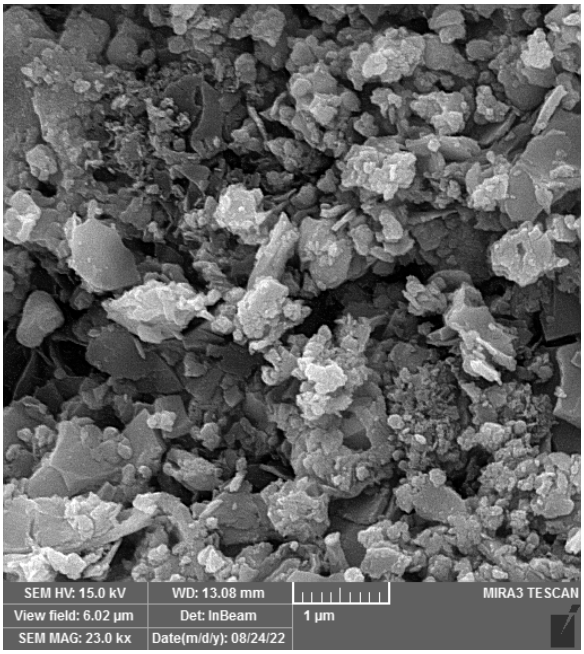
In the context of this equation where "xi" represents the influential factors and "yi" stands for the corresponding removal percentage, the RF algorithm generates a diverse set of decision trees denoted as "Ti" by employing bootstrap aggregating, commonly referred to as "bagging," on the training dataset "T" (Eftekhari et al., 2021). The result produced by the RF algorithm corresponds to the class that emerges as the mode among the classes (for classification tasks) or the mean prediction (for regression tasks) from the individual decision trees. All computational tasks and model training were carried out using WEKA 3.9.

Results and Discussion

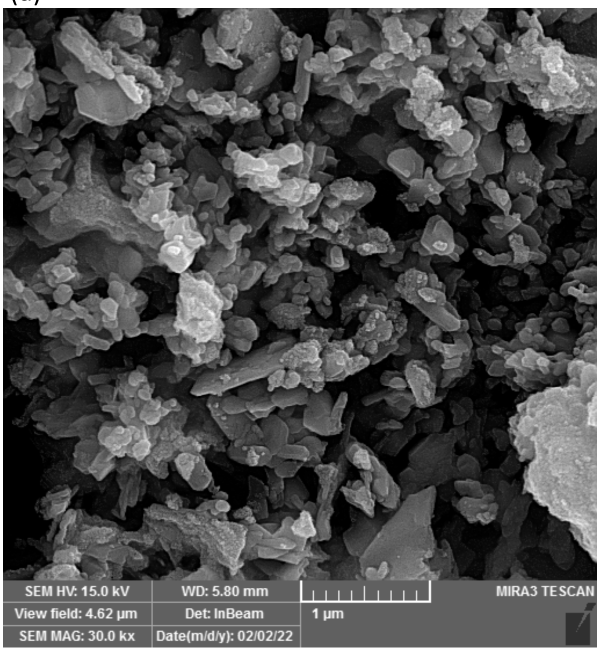
Characterisation of CTS nanoplates and GO-CTS-PANI composite

The CTS nanoplates were synthesised and characterised using XRD, FESEM, and EDX analysis. FESEM images of the synthesised CTS nanoplates are shown in **Figure 3**, while the EDX spectrum presented in **Figure 4** confirms the high purity of CTS nanoplates with peaks corresponding to Cu (0.93 and 8.04 keV), Sn (3.44 keV) and S (2.31 keV). XRD patterns of the synthesised CTS nanoplates are illustrated in **Figure 5**, which shows major diffraction peaks appearing at $2\Theta = 28.5^{\circ}$, 32.8°, 47.5°, 56.4° and 68.6°. These peaks correspond to (111), (200), (220), (311) and (400) of CTS (JCPDS no. 89-2877), indicating the CTS nanoplates possess a cubic phase (Zaman and Poolla 2020).





(a) (b)



(c)

Figure 3. FESEM images of CTS nanoplates (a-c)

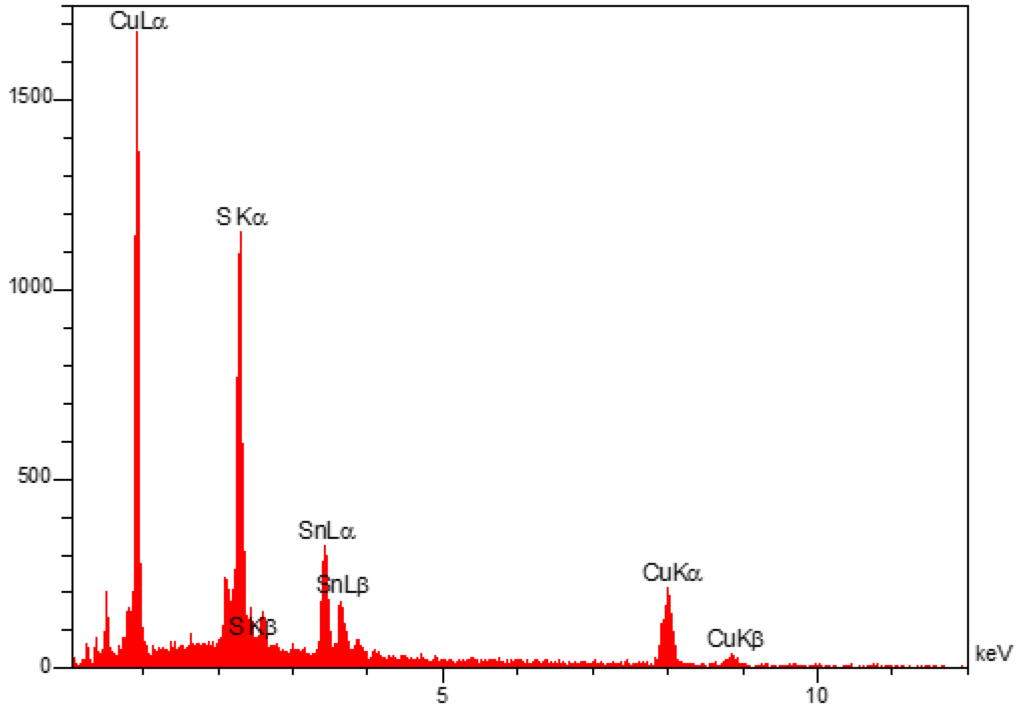


Figure 4. EDX analysis of CTS nanoplates

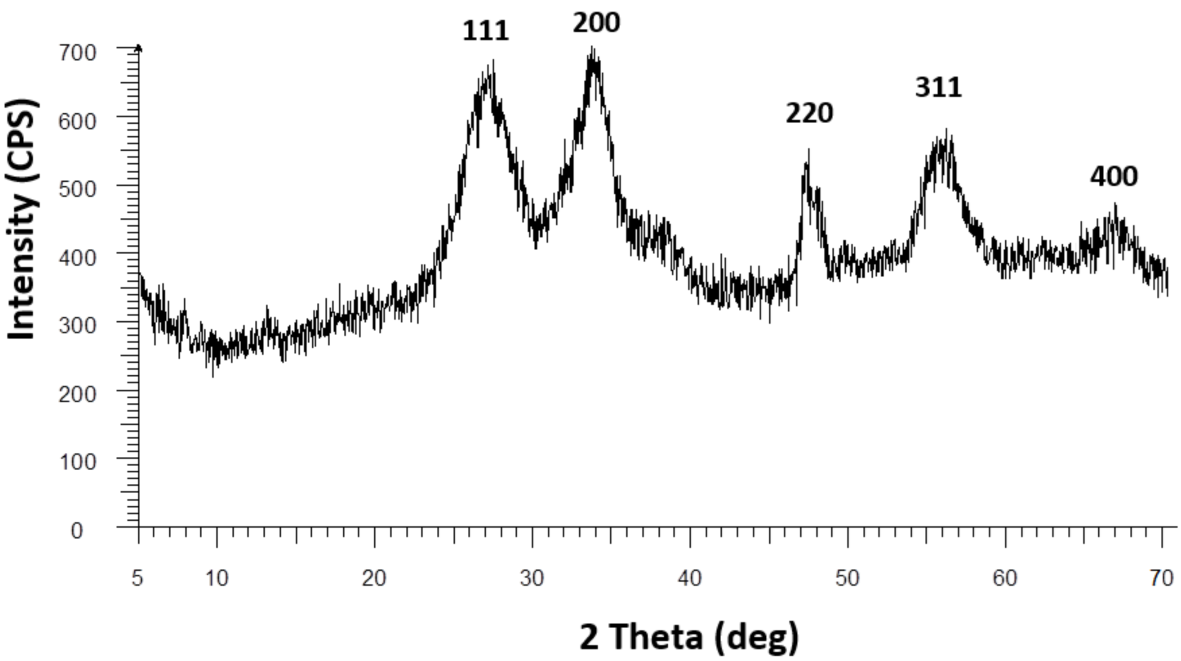
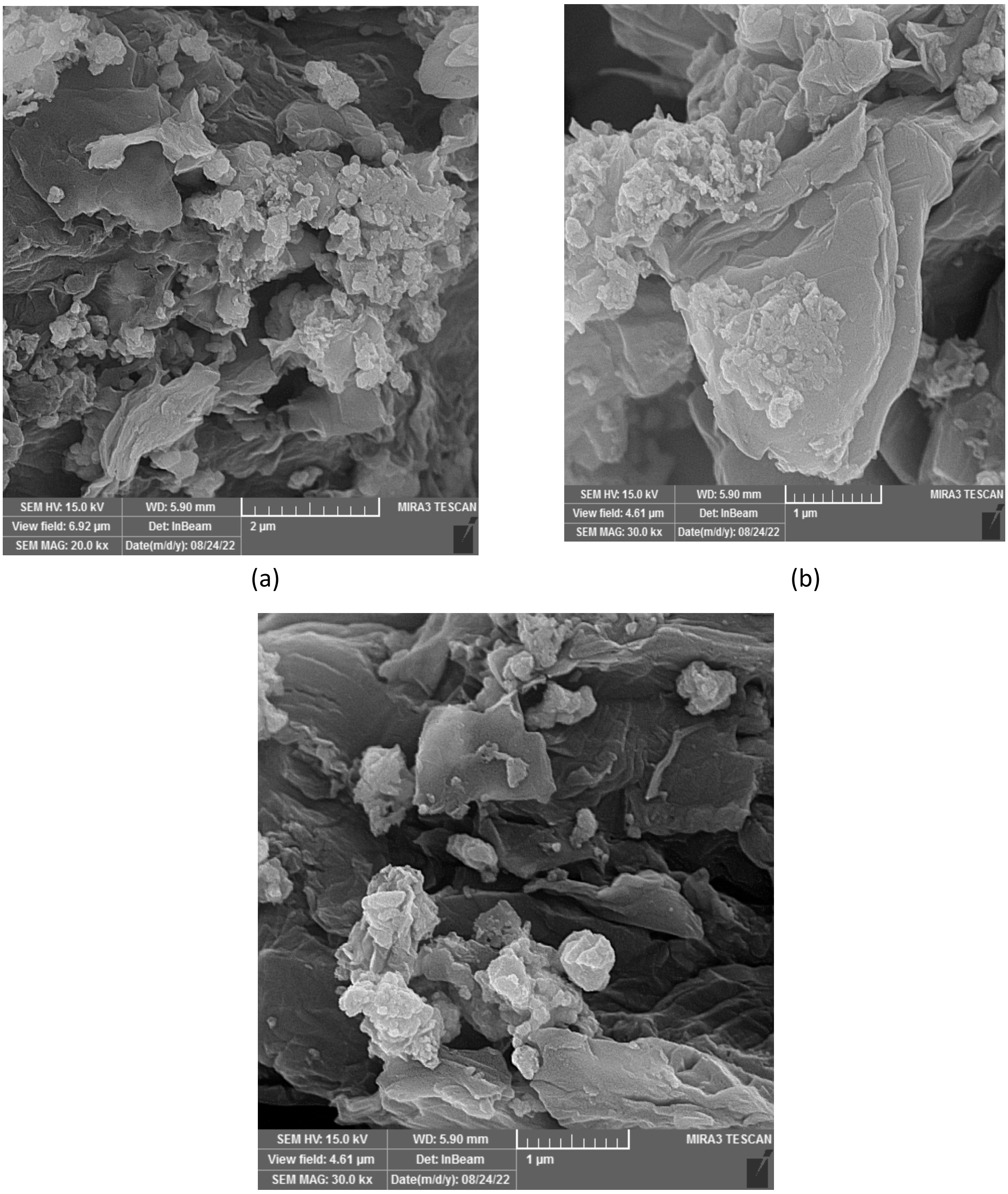


Figure 5. XRD spectrum of CTS nanoplates

Figure 6 presents FESEM images of GO-CTS-PANI composite, which indicates that GO nanosheets are occupied by CTS nanoplates and PANI. EDX analysis of the composite in **Figure 7** also shows the presence of N and O groups at 0.39 and 0.52 eV, respectively, which are attributed to PANI and GO in the synthesised composite.



(a) (b)

(c)

Figure 6. FESEM images of GO-CTS-PANI nanocomposite

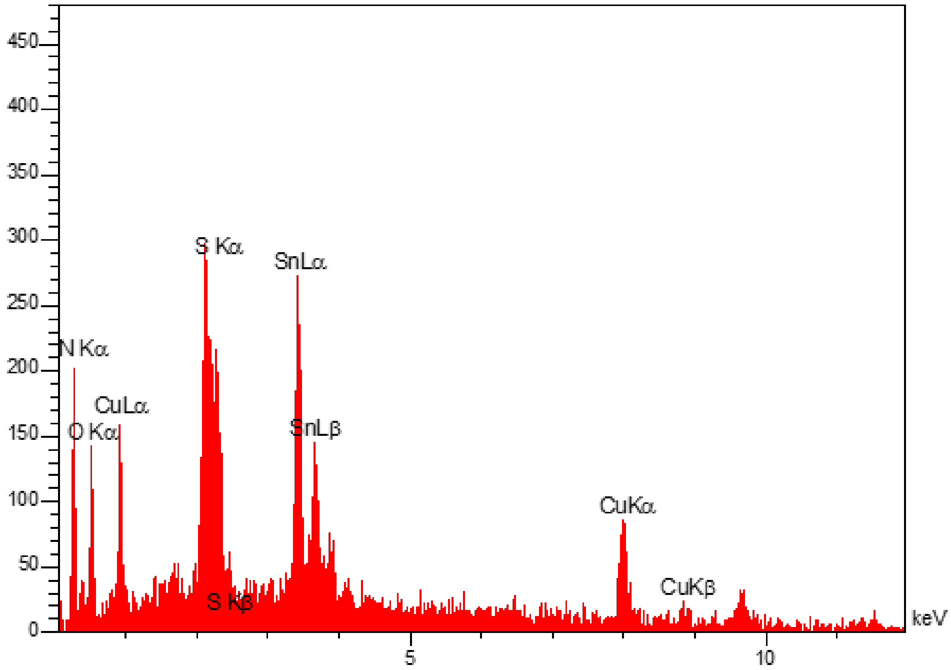


Figure 7. EDX analysis of GO-CTS-PANI composite

The GO-CTS-PANI composite was analysed using XRD in **Figure 8**. The analysis revealed clear appearance of the main peaks of CTS nanoplates in the spectrum. In addition, two peaks of GO at 2ϴ = 11.6° and 42.5° correspond to (001) and (101), respectively (Shabani-Nooshabadi and Zahedi 2019) while a broad peak at 2ϴ=20° corresponds to (100) and attributed to PANI (Liu et al., 2018).

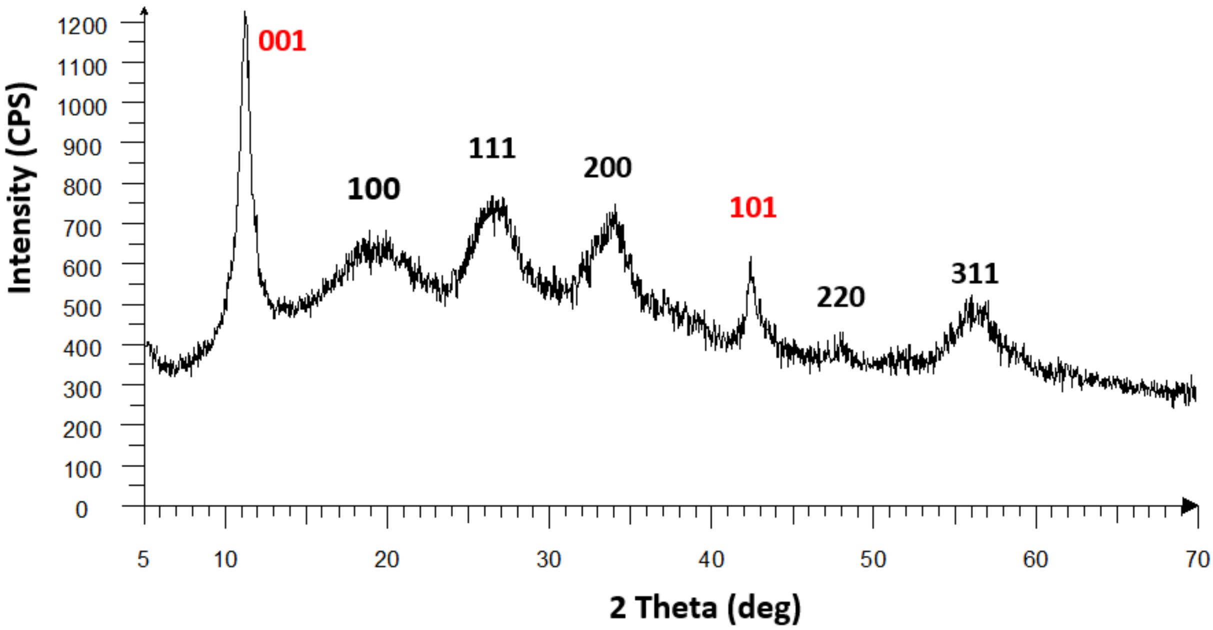
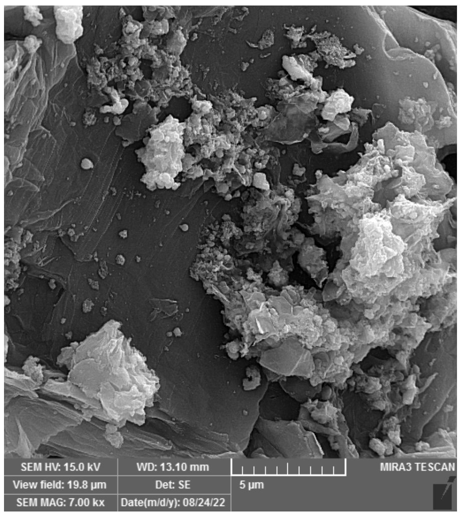


Figure 8. XRD spectrum of GO-CTS-PANI nanocomposite

MAP analysis was conducted on GO-CTS-PANI nanocomposite, and the results (**Figure 9a-e**) revealed that C (7a), Cu (7b), N(7c), O(7d), S(7e) and Sn (7f) are the main components of the synthesised GO-CTS-PANI nanocomposite.



(a)

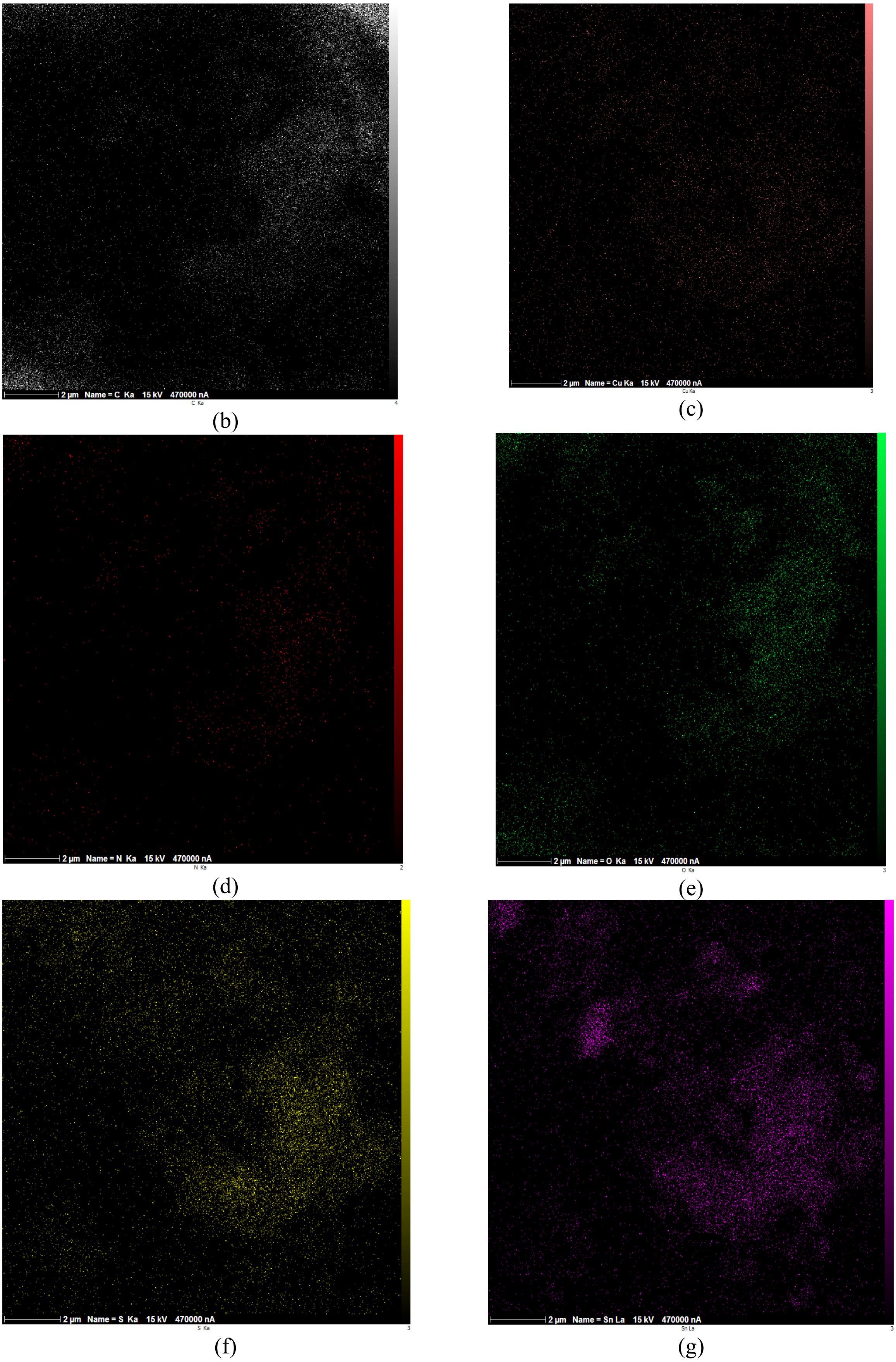


Figure 9. MAP elemental analysis of GO-CTS-PANI; distribution of mapping zone in SEM image (a) C (b), Cu (c), N(d), O(e), S(f) and Sn (g) (a-f images).

Finally, the FT-IR spectra of GO-CTS-PANI composite and CTS nanoplates are presented in **Figure 10**. The CTS spectrum shows a sharp peak at 500-750 cm^{-1} that is related to the vibration of Cu-S, Sn-S bonds. The band at 1630 cm^{-1} is due to the O-H bending of water molecules and a peak appeared at 1130 cm^{-1} could be attributed to the stretching vibration of C-N band of thiourea in the structure of CTS nanoplates. The FT-IR spectrum of GO-CTS-PANI shows the peaks at 3300 cm^{-1} (stretching of N-H, O–H), 1050 cm^{-1} (C–O of hydroxyl group), 1730 cm^{-1} (C=O) and 1650 cm^{-1} (C=C). Moreover, the intense peak of Cu-S and Sn-S (at 500-750 cm^{-1}) in CTS nanoplates is reduced after modification by GO-PANI.

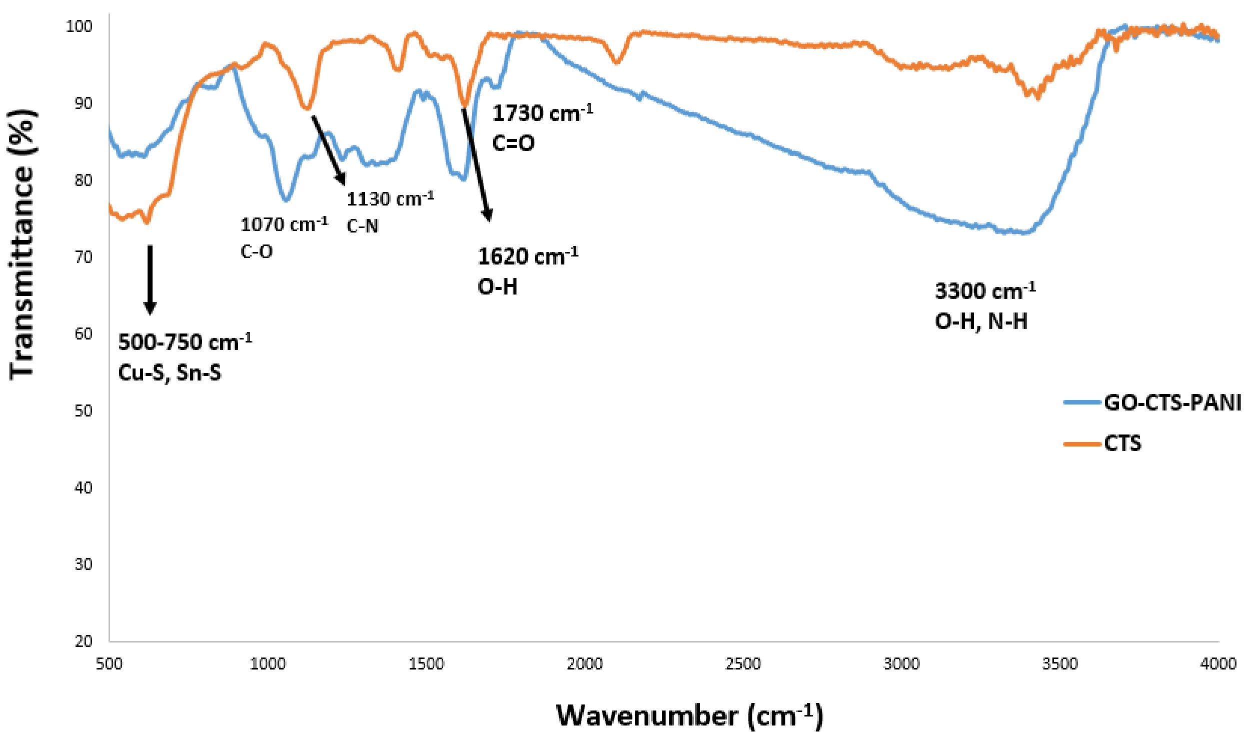


Figure 10. FT-IR spectrum of the synthesised CTS nanoplates and GO-CTS-PANI

Optimisation of parameters

To optimise effective features including pH, adsorbent amount (M), and contact time, Box-Behnken method was applied using Design Expert Version 7.0.0 for 50 mg L^{-1} Hg^{2+} ion. The range of each parameter in the Design of Experiments (DOE) as well as the statistical analysis outcomes of experiments are presented in Table 1. The responses obtained from the experiments are distributed between 36% and 95%. Also, the model follows polynomial and quadratic equation for fitting effective features as per removal percentage of Hg^{2+}. Likewise, according to Table 1, it can be concluded that there is spread distribution of Hg^{2+} ion purification from water samples in different conditions of adsorption operation process. Therefore, finding the optimum condition will be valuable in viewpoints of water treatment efficiency.

Table 1. The limitations of DOE in this study

Factor	**Name**	**Units**	**Type**	**Low Actual**	**High Actual**	**Low Coded**	**High Coded**	**Mean**	**Std. Dev.**	
A	pH		Numeric	2	7	-1	1	4.5	1.714986	
B	M	mg	Numeric	5	15	-1	1	10	3.429972	
C	Contact time	min	Numeric	10	50	-1	1	30	13.71989	
Response	Name	Units	Obs	Analysis	Minimum	Maximum	Mean	Std. Dev.	Ratio (max/min)	Model
Y1	RP	%	17	Polynomial	36	95	59.47059	17.9	2.58	Quadratic

Table 2 displays various statistical metrics, including Standard Deviation, R-Squared, Adjusted R-Squared, Predicted R-Squared, and Press, for four distinct models: linear, 2FI, quadratic, and cubic. As indicated by the information in Table 2, the quadratic model (as described in Equation 3) exhibits superior performance, with an R-Squared value of 0.99 and a Predicted R-Squared value of 0.94, outperforming the other models. Nevertheless, it's worth noting that the Predicted R-Squared value can be further enhanced by incorporating machine learning computations.

Table 2. The curve fitting regression outcomes in different mathematical models.

Source	Std. Dev.	R-Squared	Adjusted R-Squared	Predicted R-Squared	PRESS	
Linear	7.412232	0.869001	0.838771	0.741765587	1407.955	
2FI	8.351559	0.872074	0.795318	0.409168432	3221.353	
Quadratic	2.339108	0.992975	0.983944	0.942684058	312.5	Suggested
Cubic	2.280351	0.996185	0.98474			

$$\mathbf{RP} = -3.38-2.36*\ pH+5.82*M + 1.07*\ \text{Contact time}+0.14*\ pH * M+ 0.015*\ pH * \text{Contact time}+ 7.5E\text{-}003*\ M * \text{Contact time}+ 1.12*\ pH^2-0.29*\ M^2-0.018*\ \text{Contact time}^2 \quad (3)$$

The Analysis of Variance (ANOVA) results presented in Table 3 demonstrates that the designed model (Equation 1) is significant with a P-value <0.0001 and the error value in prediction (lack of fit) is insignificant indicating the validity of the equation. Among the three parameters (pH, M, and contact time), pH has the smallest P-value (<0.0001) and largest F-value (842.19). Between the other two factors, the mass of adsorbent has more importance (P-value = 0.0039) that the contact time (P-value = 0.0462).

Table 3. The results of ANOVA practices in this study

Source	Sum of Squares	Mean Square	F-Value	P-value	
Model	5413.9	601.54	109.9436	< 0.0001	significant
A-pH	4608	4608	842.1932	< 0.0001	
B-M	98	98	17.91123	0.0039	
C-Contact time	32	32	5.848564	0.0462	
AB	12.25	12.25	2.238903	0.1782	
AC	2.25	2.25	0.411227	0.5418	
BC	2.25	2.25	0.411	0.5418	
A^2	207.79	207.79	37.97	0.0005	
B^2	235.26	235.26	42.99	0.0003	
C^2	235.26	235.26	42.99	0.0003	
Residual	38.3	5.47			
Lack of Fit	17.5	5.83	1.12	0.4395	not significant
Pure Error	20.8	5.2			
Cor Total	5452.2				

The statistical distribution of results is presented in **Figure 11** (Normal% probability via internally studentised residuals). Based on the results the normality of experimental outputs of the DOE were found to be normal all the data are located within the normal diagram according to the declared scheme. A normally distributed dataset implies that the mean and standard deviation of the data are well-defined, which can aid in the design and optimisation of the system. Additionally, engineers can use this information to make informed decisions about the system, such as setting appropriate tolerances for manufacturing processes or determining the expected variability in system performance. Overall, the normality of the experimental outputs is a useful piece of information for engineers to consider when analysing and designing systems. **Figure 12**(a-c) shows the outcomes of the dual sensitive evaluation of effective experimental factors for adsorption of Hg^{2+} onto GO-CTS-PANI. **Figure 12a** demonstrates the influence of pH and amount of adsorbent on the recovery percentage of Hg^{2+}.

The findings suggest that elevating the pH level results in an augmentation of the removal percentage (RP) of Hg^{2+}, reaching its peak effectiveness at around pH 6.5-7. This notable enhancement in RP as pH increases is likely attributed to the deprotonation of functional groups like carboxyl, sulfur, and N-H on the adsorbent, enhancing their interaction with Hg^{2+} (Anirudhan et al., 2015; Gao et al., 2021). Conversely, the lower RP of Hg^{2+} in acidic solutions (pH<5) is linked to the protonation of S-atoms in CTS nanoplates, protonation of hydroxyl groups, incomplete dissociation of carboxylic acid groups (which have pKa values around 5) on GO, and protonation of -NH groups on PANI, leading to electrostatic repulsion between Hg^{2+} ions. Within the pH range of 6–7, Hg^{2+} predominantly exists as $Hg(OH)_2$ (approximately 79%) and $HgOH^{+}$ (approximately 10%) (Anirudhan and Shainy 2015). According to the Pearson rule, interactions are more favourable between hard acids and hard bases, and soft acids and soft bases (Santhana Krishna Kumar et al., 2013). Additionally, considering that neutral molecules are softer acids compared to metal cations, the interaction between Hg^{2+}

species becomes more favourable at higher pH values. Regarding the influence of the parameter "M" on RP, an increase in "M" enhances the RP of Hg^{2+} because it provides more available active sites for interaction with the analyte. However, a further increase in the "M" parameter eventually diminishes the RP, primarily due to the aggregation of the adsorbent (Eftekhari et al., 2020). **Figures 12b** and **12c** depict the effects of contact time, "M," and pH on the RP of Hg^{2+}, with the results showing that an extended contact time leads to an improved RP of Hg^{2+}. **Figure 13** shows the EDX spectrum of GO-CTS-PANI adsorbent after adsorption of Hg^{2+} that shows a peak of the adsorbed Hg^{2+} at 9.9 keV. The obtained results clearly shows that Hg^{2+} ions effectively adsorbed onto the GO-CTS-PANI adsorbent.

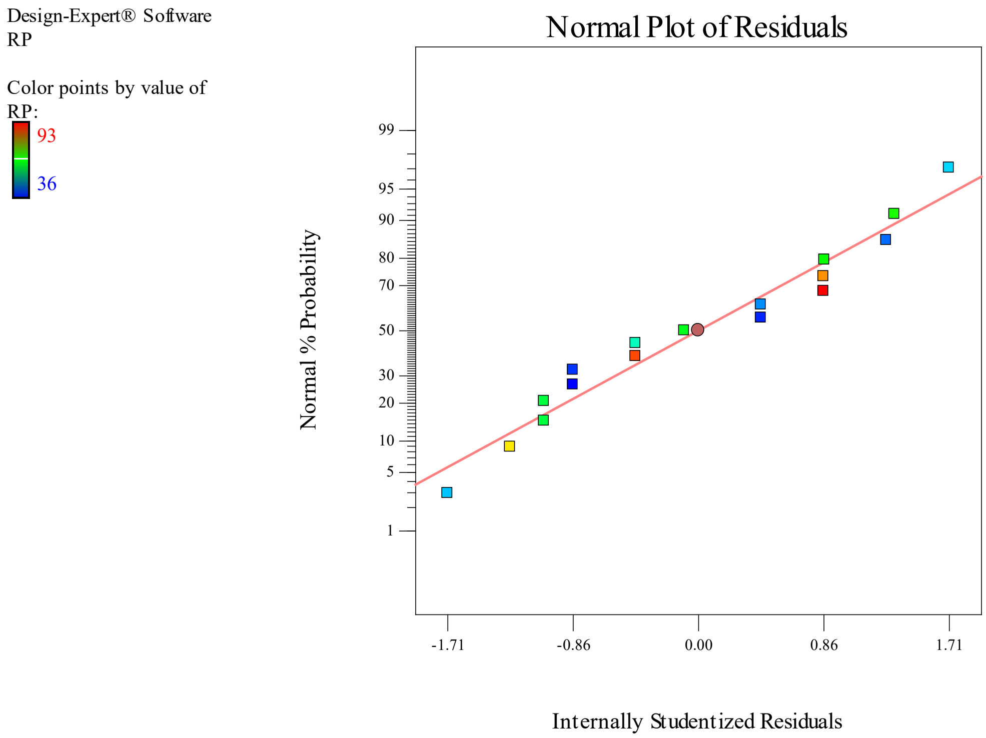
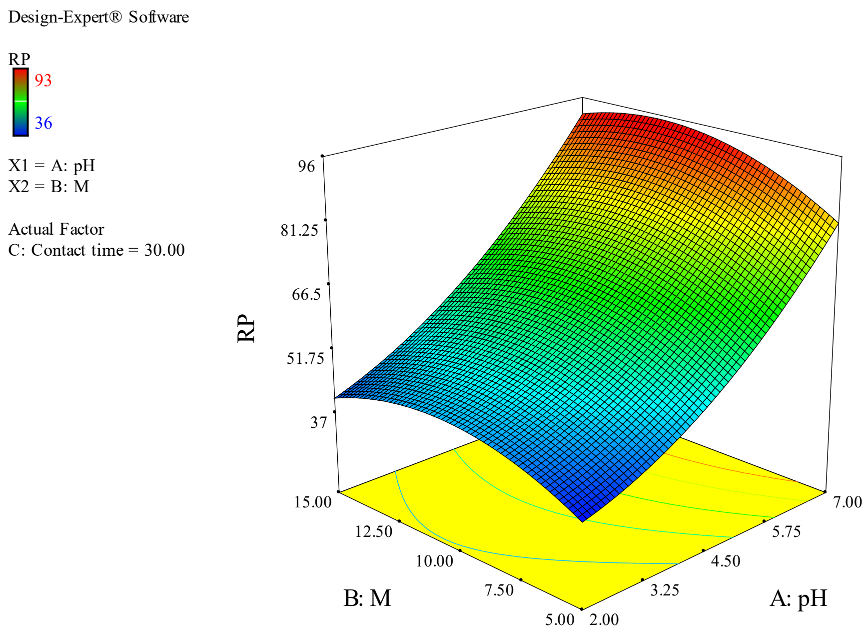
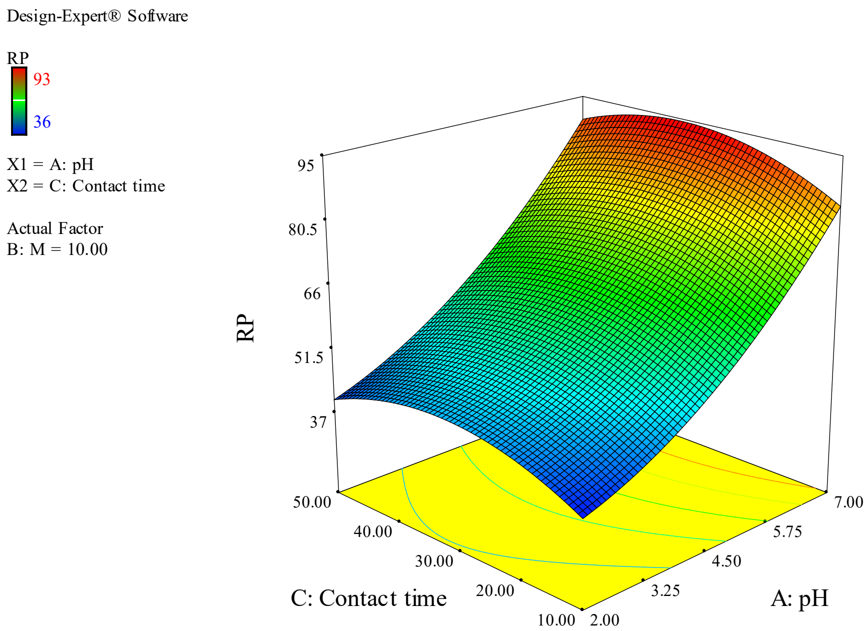


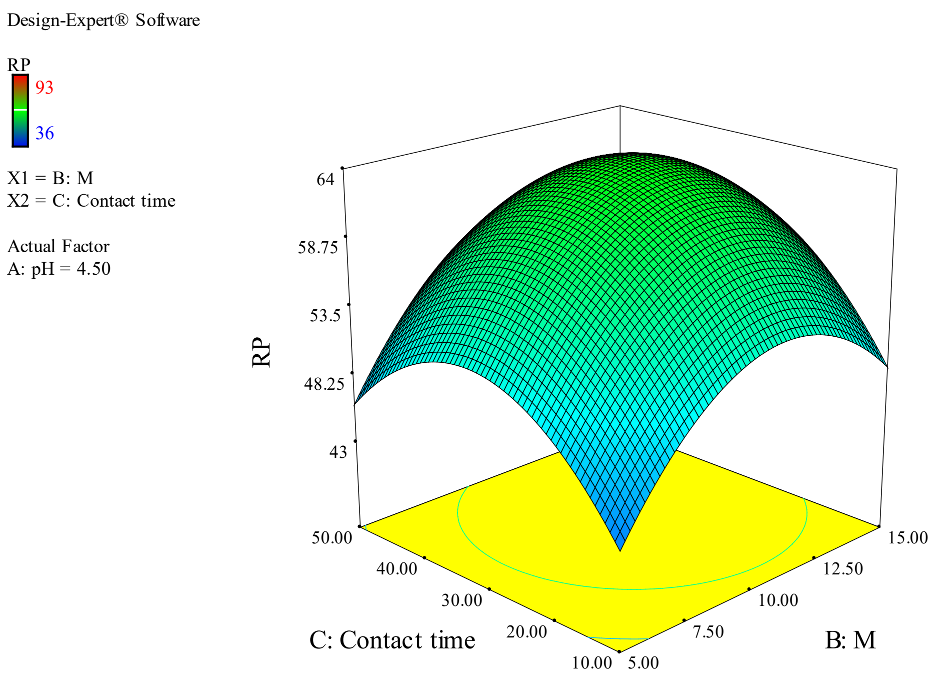
Figure 11. The normal distribution of experimental outcomes in this study


Design-Expert® Software
RP
93
36
X1 = A: pH
X2 = B: M
Actual Factor
C: Contact time = 30.00
RP
96
81.25
66.5
51.75
37
15.00
12.50
10.00
7.50
5.00
B: M
2.00
3.25
4.50
5.75
7.00
A: pH

(a)


Design-Expert® Software
RP
93
36
X1 = A: pH
X2 = C: Contact time
Actual Factor
B: M = 10.00
RP
95
80.5
66
51.5
37
50.00
40.00
30.00
20.00
10.00
C: Contact time
2.00
3.25
4.50
5.75
7.00
A: pH

(b)



(c)

Figure 12. The sensitive analysis of the studied parameters on RP of Hg^{2+} (50 mg L^{-1}) (a-c).

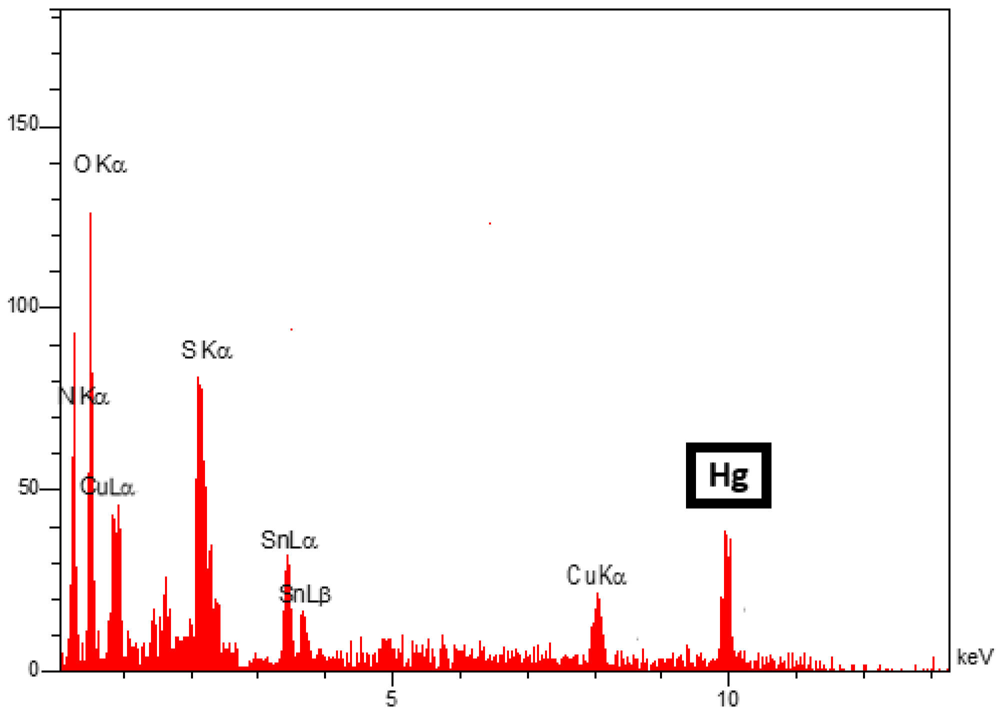


Figure 13. EDX analysis of GO-CTS-PANI after adsorption of Hg^{2+} ions.

After conducting sensitive analysis and mathematical modelling using Box-Behnken model, the optimal values of the effective factors are computed. The results (Table 4) show that the maximum performance (removal percentage as RP) for removing Hg^{2+} from water samples using GO-CTS-PANI is 95%, indicating the best operational efficiency. Therefore, the optimal performance can be obtained based on optimal features of pH of 6.5, M=12 mg and contact time of 30 min. These effective features are also depicted in **Figure 14** based on the desirability. The contours in the figure show that the maximum desirability for predicting the optimal conditions is achieved with high levels of pH and intermediate values of M.

Table 4. The optimal suggestions of effective features based on RP% in this study.

pH	M (mg)	Contact time (minutes)	RP (%)	Desirability
6.59	10.39	40.59	97	1.000
6.56	10.42	39.18	97.6633	1.000
6.50	12.07	30.38	98.3089	1.000

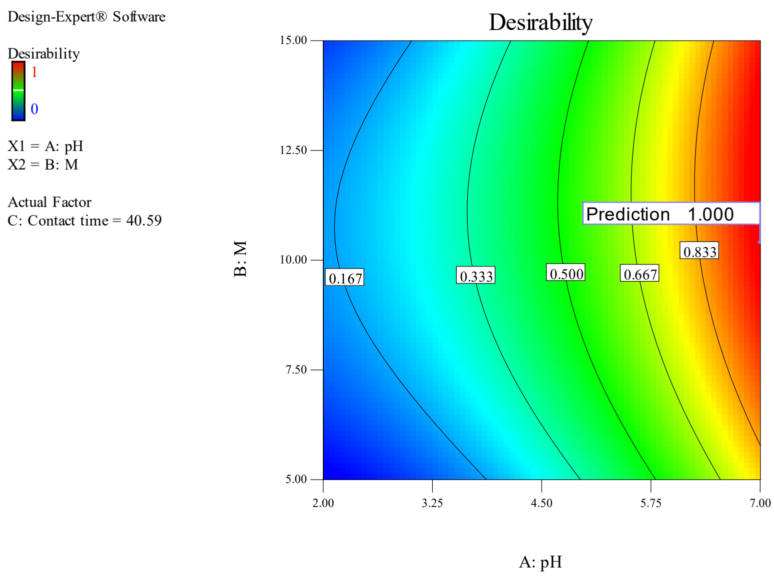


Figure 14. The contours of desirability fluctuations

Adsorption mechanism

Figure 15 shows the mechanism of Hg^{2+} adsorption onto the GO-CTS-PANI adsorbent. The figure shows that there are three main interactions between adsorbent and Hg^{2+} ions, which include: (1)- electrostatic interaction between dissociated carboxylic acid groups of GO and $HgOH^{+}$ ions (Awad et al., 2020) (2)- soft–soft interaction between Hg^{2+} and sulfur atoms of CTS (Anirudhan et al., 2015; Gao et al., 2021; Santhana Krishna Kumar et al., 2013) and (3)- chelating interaction between N and Hg^{2+} (Zeng et al., 2019).

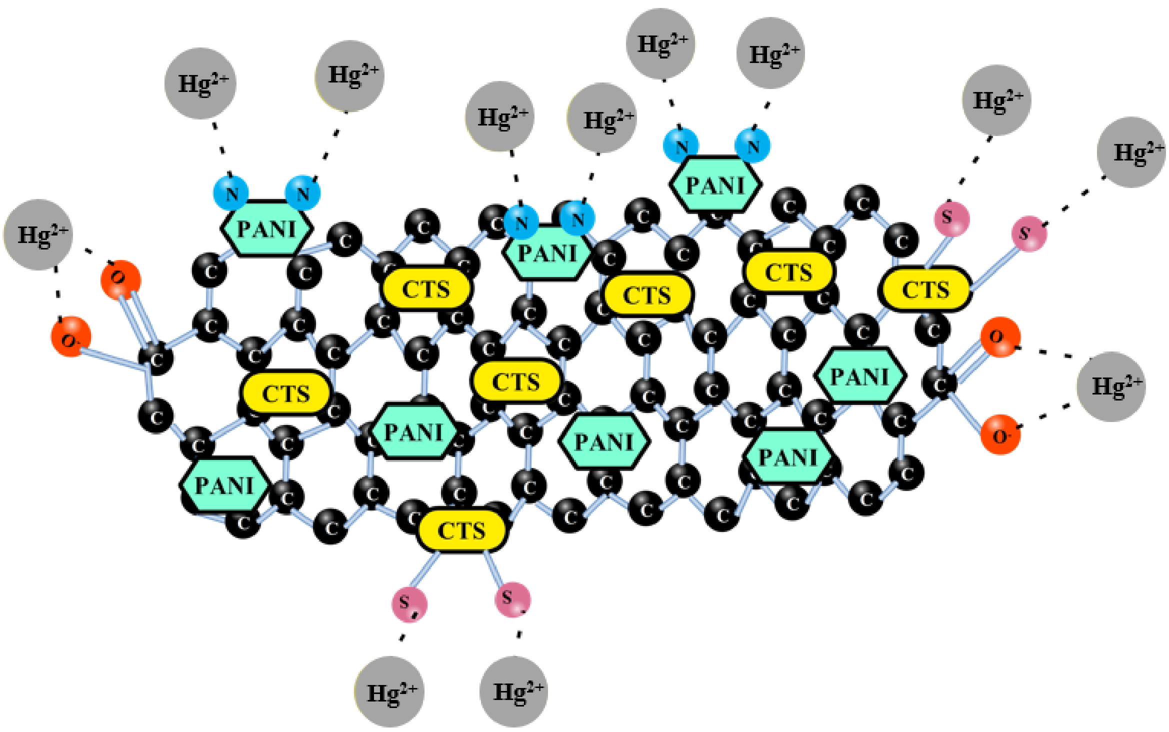


Figure 15. Adsorption mechanism of Hg^{2+} on to the GO-CTS-PANI

Adsorption isotherm

To evaluate the adsorption mechanism and determine the dominance of Freundlich and Langmuir isotherms, two-parameter, and three-parameter equations (mentioned in **Figure 16**) were applied. In the first step, two-parameter calculations are analysed as shown in **Figure 16**.

The outcomes indicate that the regression coefficient of both isotherms was over 0.95 and the precise determination of the mechanism is simply not possible. Based on two-parameter relationships, the maximum absorption capacity (Q_{max}), Langmuir coefficient (K_{ads}), K_f and n were estimated as 232.5 mg g^{-1}, 6.76 L mg^{-1}, 32.95 and 1.75, respectively. However, considering the three-parameter Sips, Khan and Toth isotherms (R^2 more than 0.99) and modelling them in Curve Expert Professional software, it was revealed that the exponential coefficients of the models did not converge to 1. Consequently, the Freundlich isotherm was found to be superior (Eftekhari et al., 2020; Eftekhari et al., 2021). It was observed that Hg^{2+} ions were adsorbed onto GO-CTS-PANI in some sequential layers and $0<1/n<1$ indicating a favourable adsorption process. **Figure 17** shows that in Temkin model, b<8 KJ mol^{-1}, and according to the Dubinin-Radushkevich (D-R) equations, E<8 KJ mol^{-1}. Therefore, the adsorption of Hg^{2+} ions onto GO-CTS-PANI is physically in nature. The D-R isotherm model was used to calculate the Q_m and K factors which were found to be 102 mg g^{-1} and 2E-07, correspondingly (Eftekhari et al., 2020).

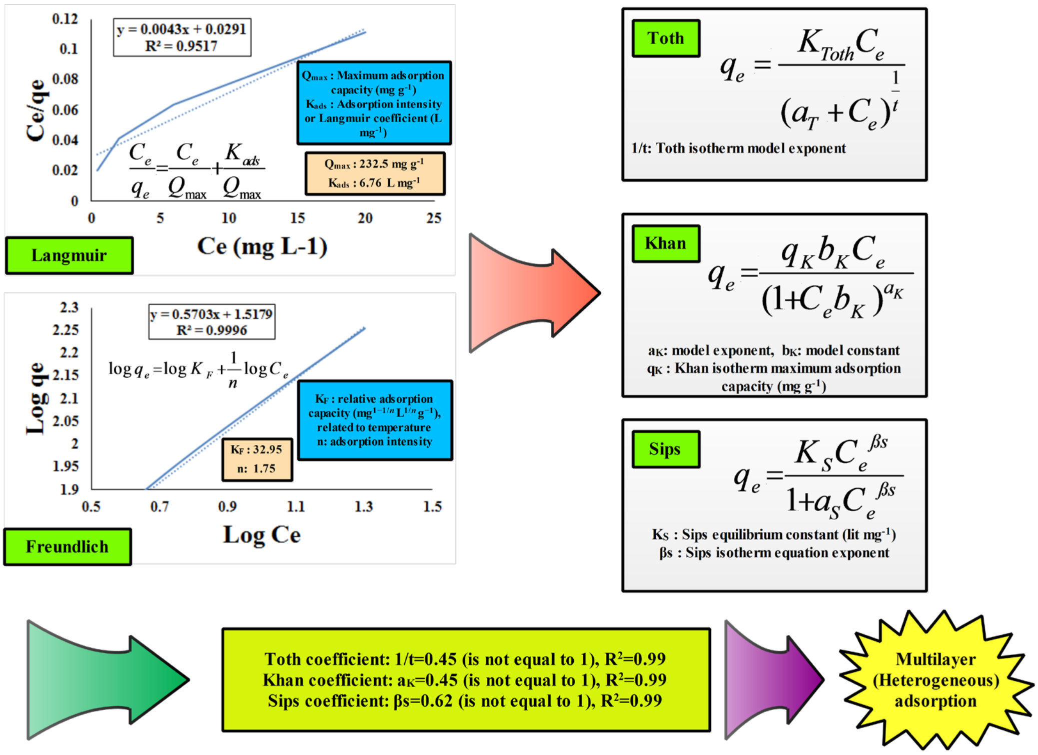


Figure 16. The computational model of Hg^{2+} adsorption onto GO-CTS-PANI.

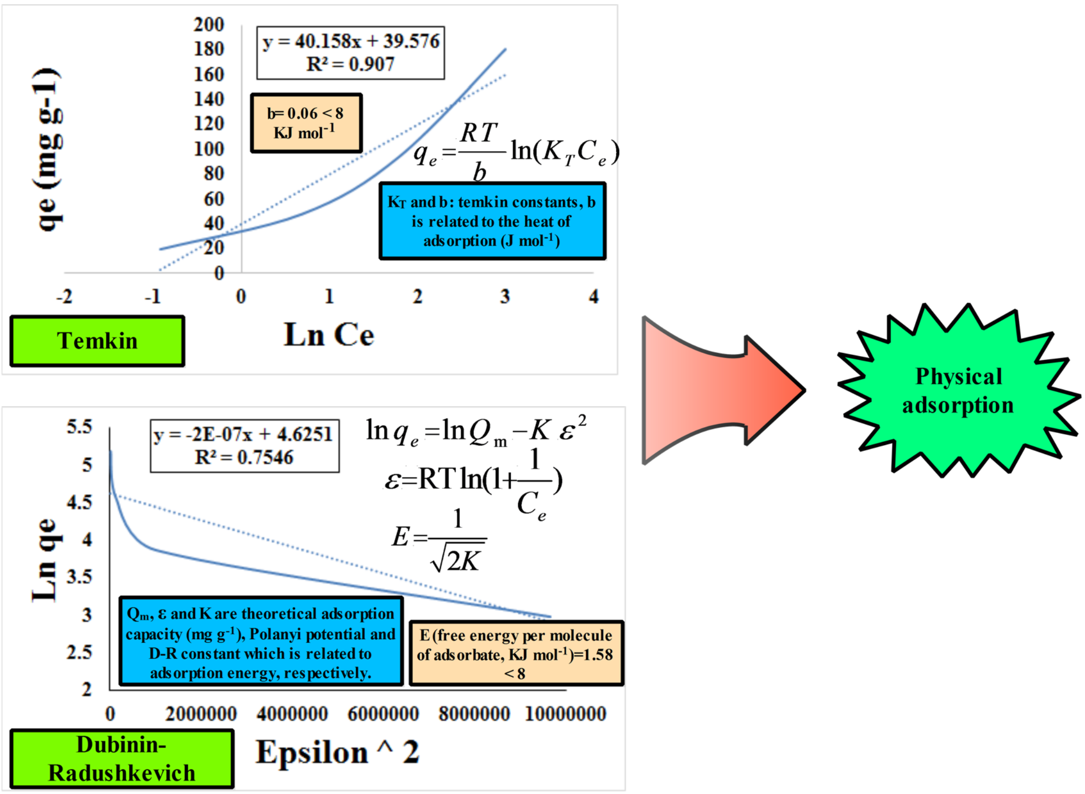


Figure 17. The physical, chemical, or intra-particle mechanism of Hg^{2+} adsorption onto GO-CTS-PANI.

Adsorption kinetic

Figures 18 and **19** demonstrate the results of Hg^{2+} kinetic adsorption onto GO-CTS-PANI using four models: Pseudo-First-Order (PFO), Pseudo-Second-Order (PSO), Intra-particle, and Elovich. Based on the data presented in **Figure 18**, the PSO model produced a more desirable R^2 value and a smaller difference between experimental and calculated q_e values compared to the PFO model. Therefore, it can be concluded that the adsorption of Hg^{2+} onto the GO-CTS-PANI follows by the pseudo second order model with a rate of k_2=0.02 mg g^{-1} min^{-1} (R^2=0.95) (Eftekhari et al., 2020; Eftekhari et al., 2021).

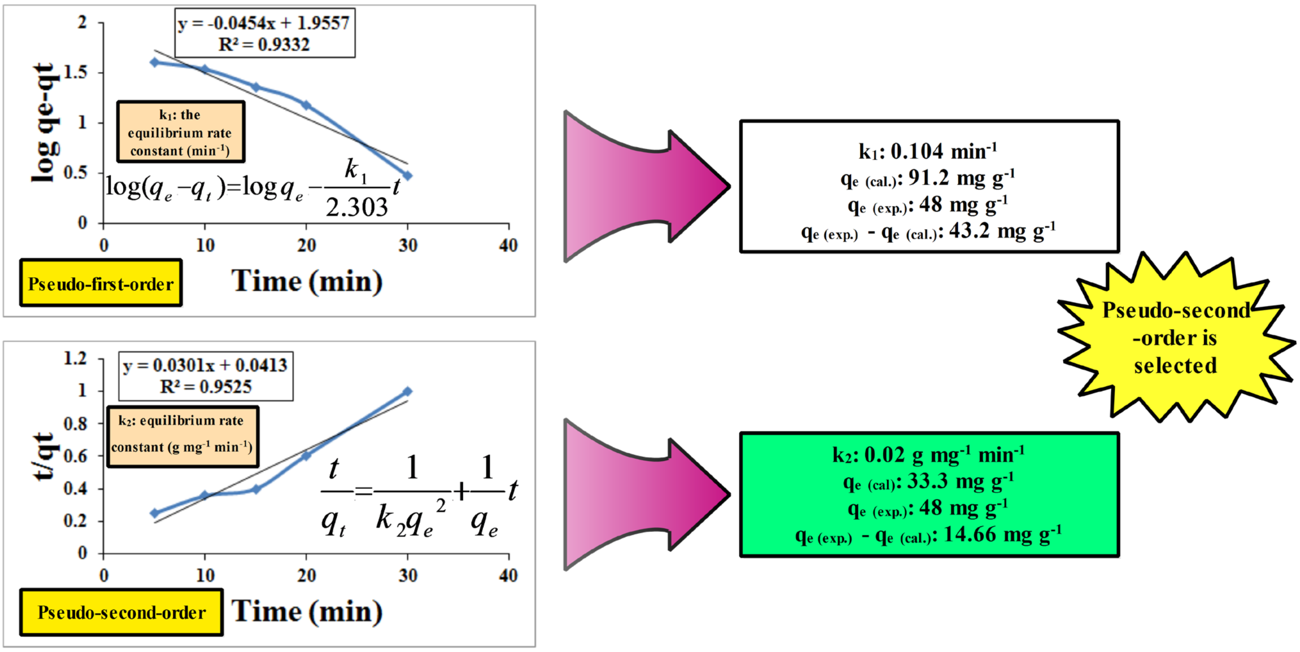


Figure 18. The outputs of kinetic reaction order and coefficient calculations in this study

Figure 19 shows that it is evident that the kinetic behaviour of Hg^{2+} adsorption onto GO-CTS-PANI can be described by both Intra-particle (R2=0.98) and Elovich (R^2=0.94) models. The Intra-particle kinetic curve has intercept of C=-20.6 indicating that both integrated intra-particle and mass transfer mechanisms play a significant role in the adsorption process

(Eftekhari et al., 2020). Moreover, the Elovich model suggests that GO-CTS-PANI has a heterogeneous surface which is consistent with the results of isothermal assessments.

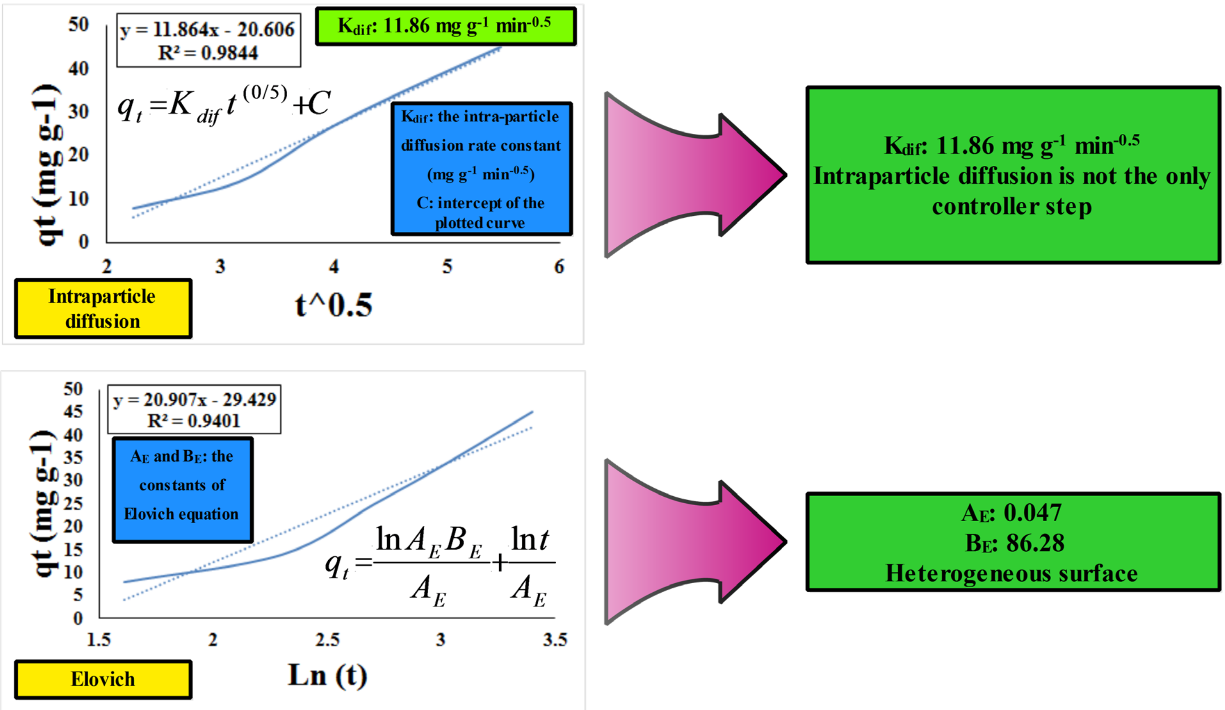


Figure 19. The outcomes of Elovich and Intra-particle kinetic models in the investigation.

Machine learning

This study also utilised machine learning practices for two purposes: (1) to improve the accuracy of prediction parameters and (2) to establish an intelligent infrastructure for online investigation of purification systems using the adsorption method. The distribution of data used in the machine learning process, carried out using the RF method is illustrated in **Figure 20**.

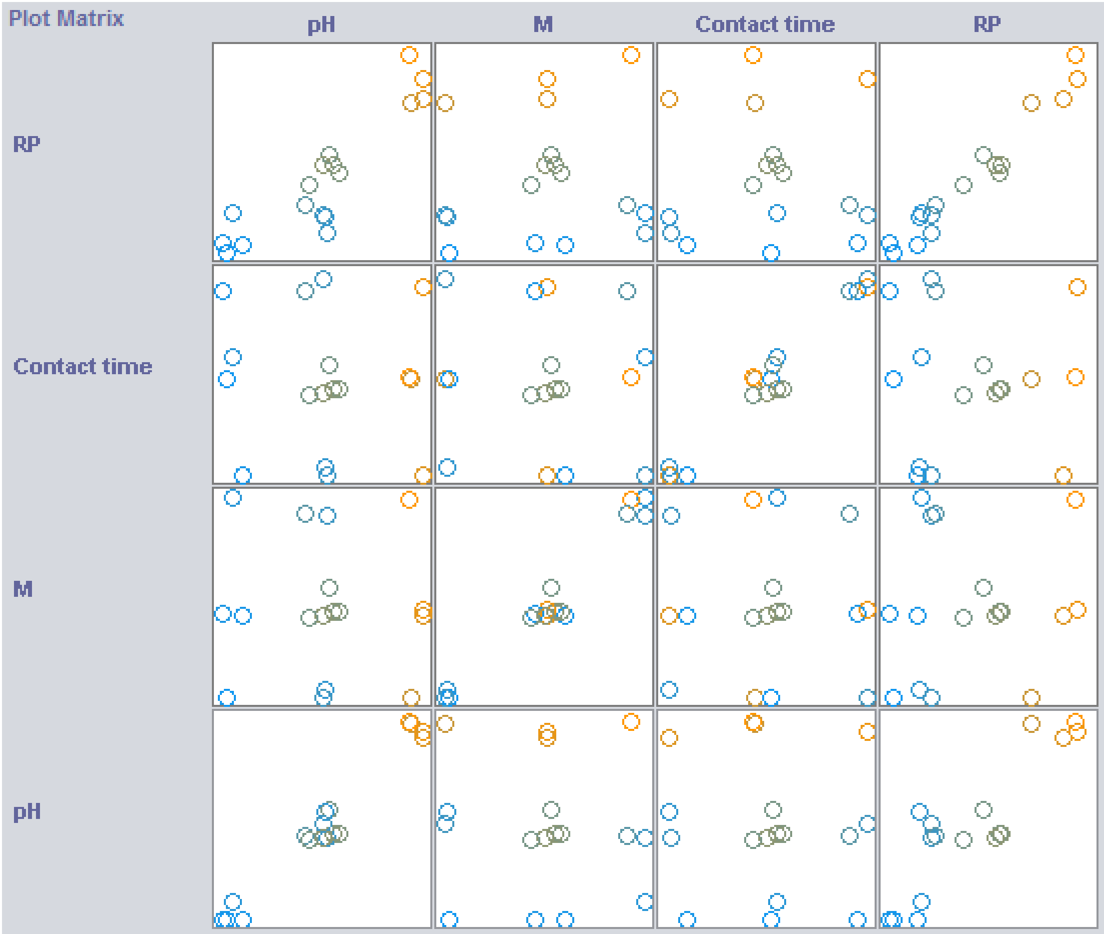
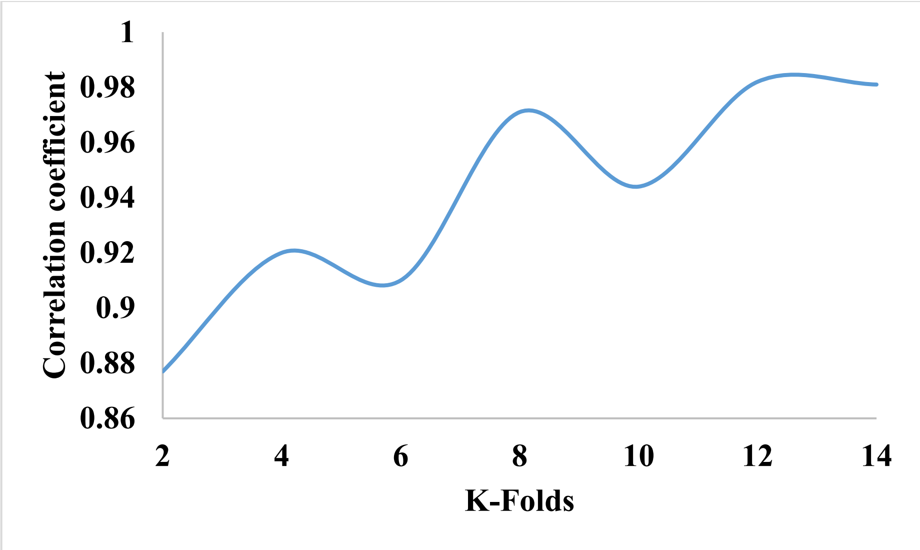
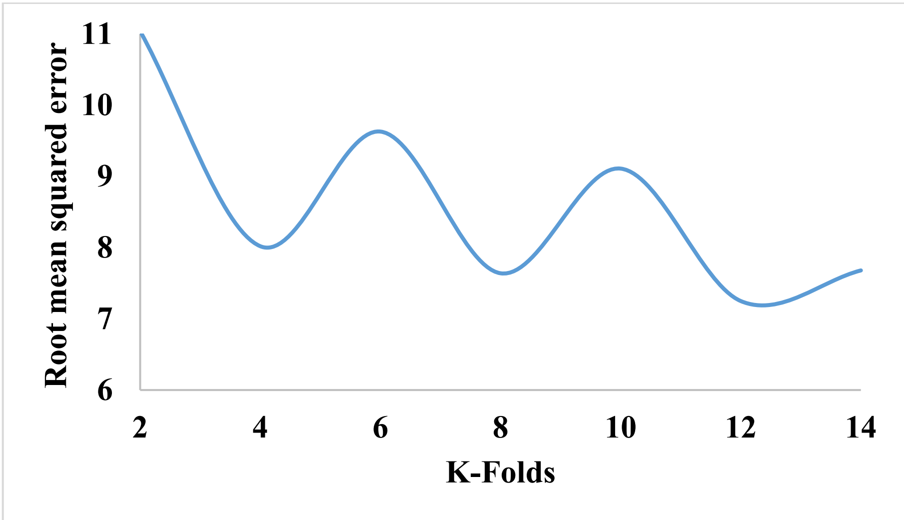


Figure 20. The distribution of data used for the machine learning modelling in this study.

Figure 21 displays the performance of the RF algorithm at different K-Folds Cross-Validation (KFCV) during training and testing process of the data. By adjusting the number of folds, the proportion of testing and training data can be determined. The correlation coefficient (**Figure 21a**) and root mean square error (**Figure 21b**) both indicate that the correlation coefficient generally increases as the number of folds increases but with some fluctuations in different steps. conversely, the behaviour of root mean square error is similar to correlation coefficient but in reverse. Therefore, the best condition is achieved at K=12 and the details are summarised in Table 5. It is worth noting that by applying the RF algorithm, the prediction performance is improved, and operation of the adsorption process can be managed automatically without the need for further examinations or other mathematical computations.



(a)



(b)

Figure 21. The effects of the number of K-folds on (a) correlation coefficient and (b) root mean square error

Table 5. The statistical indicators of the RF algorithm performance for K=12

Correlation coefficient	98.2%
Mean absolute error	6.16
Root mean square error	7.25
RAE	38.7%
RRSE	38.26%
Total Number of Instances	17

Figure 22 show the scatterplot between observed and predicted values of the removal percentage (RP). It shows that the prediction process achieved high accuracy, providing evidence of the high validity of the RF algorithm for optimising the adsorption of Hg^{2+} ions onto GO-CTS-PANI nanocomposite. The development of a Decision Support Ssystem (DSS) for the prediction of Hg^{2+} purification from water resources by adsorption process is an important achievement, and the statistical outputs of the system are highly encouraging.

The system employs the RF algorithm and takes into account critical input variables, including contact time, the quantity of adsorbent, and pH. The notably high correlation coefficient of 98.2% signifies a robust positive connection between the input variables and the outcome variable, which, in this instance, pertains to the extent of Hg^{2+} removal. This strong correlation coefficient indicates that the input variables possess substantial predictive power regarding the outcome variable, a crucial characteristic of a dependable Decision Support System (DSS). Mean Absolute Error (MAE) and Root Mean Square Error (RMSE) represent two common metrics for gauging the accuracy of a prediction model. MAE reflects the average absolute disparity between predicted and actual values, while RMSE signifies the square root of the average squared difference between predicted and actual values. In this scenario, the MAE of 6.16 and the RMSE of 7.25 indicate that the DSS's predictions closely align with the actual values. These low values underscore the high precision and reliability of the system's predictions, a vital aspect for effective decision-making.

Furthermore, Relative Absolute Error (RAE) and Root Relative Square Error (RRSE) serve as supplementary metrics for assessing prediction model accuracy. RAE quantifies the average absolute discrepancy between predicted values and actual values, normalized by the average actual value, while RRSE denotes the square root of the average squared difference between predicted values and actual values, also normalized by the average actual value. In this context, the RAE of 38.7% and the RRSE of 38.26% are relatively elevated. This implies that there exists some degree of error in the DSS's predictions. Nevertheless, it is essential to note that these values still fall within an acceptable range and do not diminish the overall reliability of the system.

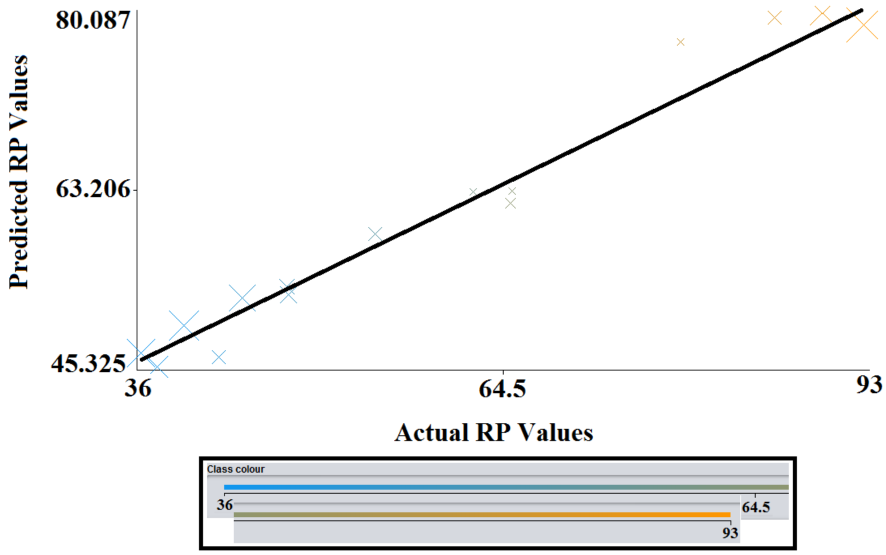


Figure 22. The scatter plot between predicted and actual values of RP% in RF algorithm (K=12)

Test of Reusability

To evaluate the potential for reusing GO-CTS-PANI, we conducted five cycles of adsorption and desorption, employing a 0.1 mol L^{-1} HCl (hydrochloric acid) solution for desorption. As depicted in **Figure 23**, following three rounds of utilizing the GO-CTS-PANI adsorbent, we observed only a marginal 6% decrease in removal percentage (RP). Nevertheless, in subsequent cycles, a more substantial reduction in RP became evident. Based on these observations, it can be inferred that GO-CTS-PANI remains effective for up to three cycles without a noteworthy decline in RP.

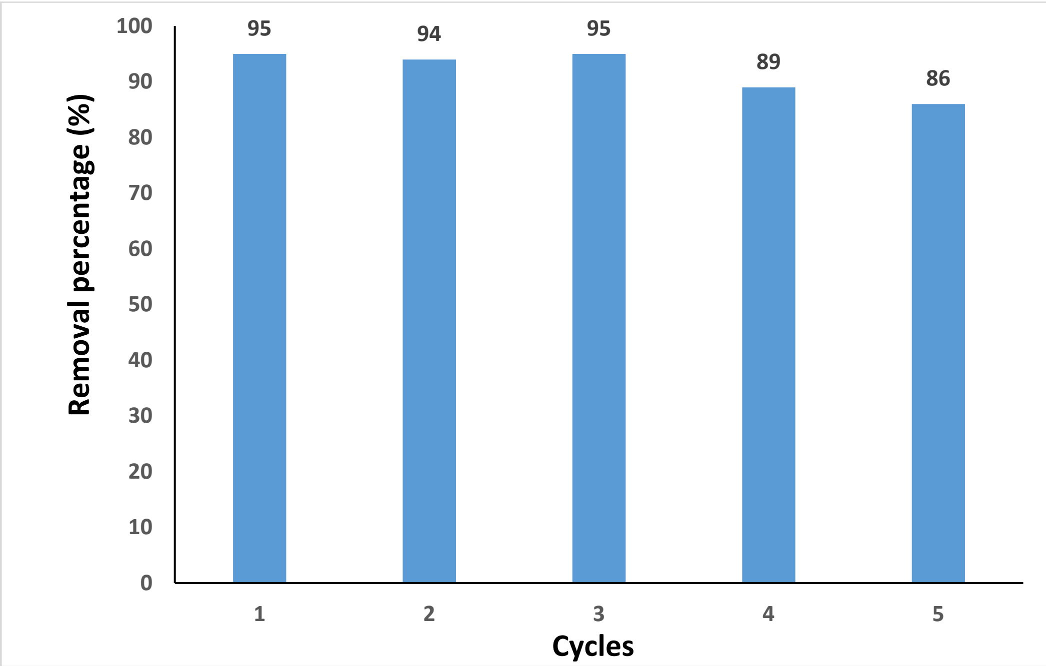


Figure 23. Results of the reusability of GO-CTS-PANI nanocomposite

Comparison with other studies

Table 6 provides a comparison between the newly developed GO-CTS-PANI composite in this study and other adsorbents employed for Hg^{2+} removal. The findings clearly illustrate that this novel adsorbent exhibits a remarkable adsorption capacity for Hg^{2+} within a short timeframe. Furthermore, as it can be effectively reused for at least three cycles without a significant reduction in removal percentage, the GO-CTS-PANI composite can be considered a highly efficient adsorbent. According to the data in Table 6, it is evident that the GO-CTS-PANI composite outperforms other adsorbents, such as palm shell activated carbon modified with ionic liquids, in terms of adsorption capacity. This enhanced performance of the GO-CTS-PANI composite can be attributed to its advantageous functional groups, including the sulfur atoms found in CTS nanoplates, the presence of nitrogen atoms in PANI, and the electrostatic interactions between the carboxylic acid groups of GO and Hg^{2+} ions. Consequently, these results strongly suggest that GO-CTS-PANI holds substantial promise as a material for effectively removing mercury from aqueous solutions.

Table 6. Comparison between GO-CTS-PANI and other adsorbents for Hg^{2+} removal

Adsorbent	Adsorption capacity (mg g-1)	Reference
2-mercaptobenzamide modified itaconic acid-grafted-magnetite nanocellulose composite	240.0	(Anirudhan and Shainy 2015)
Palm shell activated carbon impregnated with task-specific ionic-liquids	83.3	(Abu Ismaiel et al., 2013)
Polyamine modified reduced graphene oxide	63.8-59.9	(Yap et al., 2020)
Magnetic carbon nanotube	172.8	(Homayoon et al., 2017)
Mercapto-modified bentonite	19.3	(Sahan et al., 2018)
Mercaptobenzothiazole modified cellulose	204.1	(Krishna Kumar et al., 2013)
GO-CTS-PANI	232.5	This study

Conclusions

The GO-CTS-PANI composite proved effective as an adsorbent for eliminating Hg^{2+} from water samples. The optimal conditions, resulting in a 95% removal rate for 50 mg L^{-1} Hg^{2+}, were determined as follows: pH= 6.5, 12 mg of GO-CTS-PANI adsorbent, and a 30-minute contact period, employing the Box-Behnken method. The adsorption process exhibited a multilayer adsorption mechanism with physical interactions on the surface, as evident from conventional calculations. Kinetic analysis revealed that the adsorption reaction adhered to the PSO equation. Sensitivity analysis identified pH as the most influential factor impacting the adsorption process. Both RSM and machine learning techniques, specifically the RF method, proved effective for optimizing the adsorption process and predicting its efficiency, respectively. Furthermore, the GO-CTS-PANI nanocomposite demonstrated its reusability through five cycles of adsorption/desorption, with merely a 6% reduction in removal efficiency observed after three cycles. Ultimately, this study underscores the exceptional efficiency and reusability of the GO-CTS-PANI composite as an adsorbent for Hg^{2+} removal, showcasing its potential for future applications in water purification.

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Ethical approval

Not applicable.

Consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

The authors declare no competing interests.

Contributions

Sara Enferadi: data curation, methodology; Mohammad Eftekhari: data curation, methodology, supervision, conceptualization, writing—review and editing; Mohammad Gheibi: methodology, software, writing—review and editing; Nikoo Nabizadeh Moghaddam: data curation, methodology; Stanislaw Wacławek: writing—review and editing, and supervision; Kourosh Behzadian: data curation and conceptualization, supervision, writing—review and editing.

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