Palm shell activated carbon impregnated with task-specific ionic-liquids as a novel adsorbent for the removal of mercury from contaminated water

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HIGHLIGHTS

• PSAC modified with task-specific ionic liquid was used as a novel adsorbent.
• PSAC grafted with TOMATS enhances the adsorption of Hg(II) ions.
• The maximum adsorption of mercury at room temperature was 83.33 mg/g at pH 8.
• The higher removal of Hg indicates the chemisorptions nature of adsorption process.

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ABSTRACT

In this study, palm shell activated carbon modified with task-specific ionic liquids was used as a novel composition for the removal of mercury from aqueous solutions in water samples through a batch-adsorption technique. The effect of pH, adsorbent dosage, equilibrium time, temperature and initial concentration of mercury ions on the removal efficiency were examined. The maximum adsorption of mercury at room temperature was 83.33 mg/g at pH 8 with a contact time of 3 h and an initial concentration of 10–200 mg/L. The experimental data were fitted well with the linear form of Langmuir model. Adsorption kinetics followed a pseudo-second-order model. The calculated activation energy for adsorption was 68.21 kJ/mol, indicates that the adsorption process involves some chemical forces and occurs by a chemisorption process. Thermodynamic parameters, including \( \Delta H^\circ \), \( \Delta S^\circ \) and \( \Delta G^\circ \) for the adsorption process of mercury from aqueous solutions onto palm-shell activated carbon impregnated with trioctylmethylammonium thiosalicylate (TOMATS) indicated that adsorption was endothermic and spontaneous process.

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1. Introduction

Heavy metals, primarily cadmium, nickel, copper, lead, zinc, mercury, arsenic and chromium, reach the environment through several anthropogenic sources. Low concentrations of heavy metals are toxic and harmful to humans, plants and animals due to their toxicity and non-biodegradability [1]. The contamination of water recourses by heavy metals is a serious environmental problem worldwide. Numerous metals, including mercury, cadmium, chromium, and lead, are known to be significantly toxic [2]. Mercury is one of the most toxic heavy metals in aqueous solution and is usually found in the dissolved phase at low concentrations. According to the European Water Framework Directive, mercury and its compounds are classified as one of 20 priority hazardous substances. Mercury accumulates within the human brain and causes central nervous system (CNS) effects. Consequently, the development of reliable methods for the removal of mercury in environmental samples is particularly significant. Several physical and chemical methods have been reported for the removal of mercury from aqueous solutions. The available methods include membrane separation [3–5], precipitation [6,7], solvent extraction [8,9], ion exchange [10,11], reverse osmosis [12], coagulation [13] and photo reduction [14]. However, these methods are associated with high operational costs and incomplete removal and consume either large amounts of energy or large quantities of chemicals. The adsorption technique is generally considered to be a promising method and has been studied for the removal of metals from solutions [15,16]. The adsorption method typically involves natural materials that are abundant and inexpensive. Among these materials, various adsorbents, such as modified biomaterials [17,18], modified cellulosic materials [19,20], extracellular biopolymers [21], quartz and gibbsite [22,23], zeolites [24,25], nanomaterials [26–28], carbon nanotubes [29] and activated carbon [30,31] have been investigated with respect to their adsorption of heavy metal ions from solutions.
Recent research has focused on the removal of heavy metal ions by palm shell activated carbon [32]. Palm shell activated carbon is a waste produced during palm kernel oil production, which is an important sector of the Malaysian economy. This material is readily available at low cost, has a high surface area and is of high quality. These properties make palm-shell activated a good raw material for the adsorption of heavy metals from solutions.

Recent studies have focused on the modification of the surfaces of activated carbon with chelating groups to enhance the adsorption efficiency of activated carbon toward a particular metal species from aqueous solutions [33].

Similar to activated carbon, room temperature ionic liquids (RTILs) have also recently received a great deal of attention. Ionic liquids are salts that have very low melting temperatures (close to room temperature). Ionic liquids have become an extremely popular item in recent separation and purification research due to their unique properties [34]. The properties of ionic liquids (ILs) (e.g., high polarity, conductivity, viscosity, acidity and hydrophobicity) depend on the nature and the size of their cationic and anionic species. Task specific ionic liquids are a unique subclass of ionic liquids that possess a potential spectrum of utility extending far beyond that likely for more conventional IL [35]. A widespread field of research is the use of ionic liquids (ILs) as well as task-specific ionic liquids (TSILs) for the removal of heavy metals [36,37].

In this work, palm shell activated carbon impregnated with the task-specific ionic liquid (TOMATS) was used as a novel composition for the removal of mercury from aqueous solutions.

According to the theory of hard and soft acids and bases (HSAB theory), Hg(II) is classified as a soft Lewis acid and therefore forms strong bonds with soft base ligands, such as thiol groups (SH) [38]. Therefore, palm-shell activated carbon impregnated with a task-specific ionic liquid that contains SH groups should exhibit a high adsorption capacity for mercury ions. The unique adsorption of Hg(II) ions on the impregnated palm shell activated carbon with TOMATS depends on the coordinate interaction between the TOMATS and the Hg(II) ions, which may be explained by the chelating effect of the ortho-positioned carboxylate group on TOMATS molecules grafted onto palm shell activated carbon, in addition to the known formation of metal-thiolates.

The effect of several parameters, including the pH of the solution, the adsorption dosage, the equilibrium time, the initial concentration of the solution, the weight of impregnated TOMATS and the activated carbon particle size were studied. Isotherm results and kinetic and thermodynamic parameters for the adsorption process of mercury from aqueous solutions onto impregnated palm shell activated carbon were obtained.

2. Materials and methods

2.1. Chemicals and reagents

All chemicals used were of analytical-reagent grade and de-ionised water was used for the preparation of all aqueous solutions. Commercial granular palm shell activated carbon (PSAC) produced by a physical activation process was provided by Pacific Activated Carbon, a local manufacturer in Johor Bahru, Malaysia. Activated carbon was sieved into three series, with particle sizes that ranged from 0.50 to 0.60, 0.60 to 0.85 and 1.4 to 1.7 mm. The activated carbon was subsequently washed with distilled water to remove impurities and then dried in an oven at 110 °C for 24 h. Metal salts were purchased from Merck, and aqueous metal solutions were prepared by the dissolving of appropriate quantities of metal salts in de-ionised water. Trioctylmethylammonium thiosalicylate (TOMATS) was purchased from Sigma-Aldrich. The pH levels of the solutions were adjusted by the addition of the appropriate amount of hydrochloric acid (1 M HCl) or sodium hydroxide (2 M NaOH).

2.2. Analytical methods

Mercury was analysed using inductively coupled plasma atomic emission spectrometer ICP-AES (PerkinElmer, model ICP Optima 7000DV). All pH measurements were made performed with a pH/ion meter (Metrohm-781, Germany) and pH module (Metrohm-867).

The surface morphology and elemental analysis of the palm-shell activated carbon were obtained using an AURIGA field-emission scanning electron microscope cross-beam workstation (Carl Zeiss) equipped with an EDAX unit (AMETEK, Advanced Microanalysis Solutions) operated at an accelerating voltage of 25 kV.

2.3. Preparation of impregnated palm shell activated carbon

To prepare impregnated palm shell activated carbon with task-specific ionic liquids, 1 g of each activated carbon series and 0.00–0.3 g of TOMATS were placed into 250 mL Erlenmeyer flasks with 50 mL of methanol. The solutions were subsequently agitated on an orbital shaker at 180 rpm at a constant temperature of 25 °C for 2 days. The solutions were then evaporated, and the remaining impregnated palm-shell activated carbon was weighed. The overall loading of TOMATS onto the palm shell activated carbon was calculated from weight-loss data of virgin and impregnated palm shell activated carbon.

2.4. Adsorption experiments

To optimise the adsorption efficiency, adsorption experiments were performed at various pH levels, contact times, adsorbent doses, adsorbate concentrations and temperatures.

Adsorption experiments were performed in 250 mL Erlenmeyer flasks at different temperatures between 10 and 35 °C. In each experiment, 50 mL of Hg(II) solution with a concentration between 10 and 200 mg/L was treated with a specified amount of 0.1 g of modified activated carbon (prepared from 1 g palm-shell activated carbon with average particle sizes of 0.50–0.60 mm loaded with 0.2 g of TOMATS), and the pH was adjusted to the desired value by the addition of either 1 M HCl or 2 M NaOH, as required. The solutions were then shaken on an orbital shaker at 180 rpm for a specified period of time. The adsorbent was subsequently separated from the solution using Whatmann No. 42 filter paper. The equilibrium concentrations of Hg(II) that remained in solution were measured using ICP. The mercury uptake by the modified activated carbon was calculated as follows:

\[ q_e = \frac{V(C_o - C_e)}{m}, \]

where \( q_e \) is the amount of mercury ion adsorbed per gram of modified activated carbon (mg/g), \( V \) is the sample volume (L), \( C_o \) is the initial Hg(II) concentration (mg/L), \( C_e \) is the equilibrium Hg(II) concentration (mg/L), and \( m \) is the weight of adsorbent.

The removal percentage of mercury ions (%) from aqueous solutions was calculated as follows:

\[ \text{Removal Rate} = \frac{100(C_o - C_e)}{C_o} \]

3. Results and discussion

3.1. Effect of pH

The influence of the pH of the solutions on the removal efficiency was examined at a Hg²⁺ concentration of 80 mg/L by following the
The equilibrium concentration of mercury ions over a pH range of 1–12. The results, shown in Fig. 1, indicate that the removal efficiency remained constant in the pH range of 6–8, which can be used as the working pH range for the adsorption technique. However, outside this range, the removal of mercury ions changed significantly. The diminished removal efficiency at pH > 10 was due to the interference of OH$^-$/C$^0$ and formation of hydroxyl complexes. The removal efficiency at pH < 6 was attributed to the competitive blinding of protons to the ligands on the modified activated carbon surface. Under acidic conditions, the ligand may be protonated and thereby lose its capacity to form a complex with mercury ions.

3.2. Effect of contact time

The effect of contact time on Hg(II) uptake was studied with the particle size, initial concentration, adsorbent dose and pH kept constant. The results showed that adsorption increased rapidly during the first 3 h. After 3 h, the adsorption reached an equilibrium state. As evident from Fig. 2, 3 h contact time was required to attain adsorption equilibrium for the mercury solution. During this time, more than 93% of the mercury was adsorbed because of the initial availability of free TOMATS on the modified activated carbon surface. At equilibrium, coordinate interaction between TOMATS and Hg(II) ions occurred, and adsorption became almost constant up to the end of the experiment. It can be concluded that the binding of mercury with TOMATS is high during the initial stages and that, the reactive functional groups of TOMATS were exhausted after a certain period of time; the adsorbate (mercury) then experienced difficulty occupying the surface of the modified activated carbon.

3.3. Effect of the initial mercury ion concentration

To determine the effect of the initial mercury ion concentration on the Hg(II) removal efficiency, adsorption experiments were performed with initial Hg(II) concentrations that ranged from 10 to 200 mg/L. An amount of 0.1 g of adsorbent (prepared from 1 g palm shell activated carbon with average particle sizes of 0.50–0.60 mm loaded with 0.2 g of TOMATS), under conditions of pH 8, a stirring speed of 180 rpm, 3 h of contact time and room temperature, was used for each adsorption experiment. The percentage removal of mercury is given in Fig. 3, which shows that the percentage removal of Hg(II) remained approximately constant at initial Hg(II) concentrations of 10–80 mg/L. Subsequently, from 80 to 200 mg/L, the percentage of Hg(II) removal decreased with increased initial mercury concentration because, at lower concentrations, a greater number of active sites are present that mercury ions can easily occupy. However, at higher concentrations, a sufficient number of active sites for mercury ions to occupy are not available. Consequently, Hg(II) ions are not completely adsorbed from the solution due to the saturation of the binding sites.

3.4. Adsorption isotherms models

In view of the findings of the previous section, the adsorption equilibrium was investigated in experiments performed over 3 h at an initial pH of 8. The results are shown in Fig. 4, in which $q_e$ is the amount of mercury adsorbed, in mg/g, and $C_e$ is the concentration of mercury in the solution.

The equilibrium adsorption isotherms are some of the most important data for determining the mechanism of Hg(II) adsorption on the modified palm shell activated carbon. Several isotherm models have been used to describe experimental data for adsorption isotherms. However, among these, three different appropriate
isotherm models were selected for this work for the analysis of the equilibrium data: the Langmuir, Freundlich, and Dubinin and Radushkevich isotherm models. The Langmuir model is the simplest theoretical model for monolayer adsorption onto a surface with a finite number of identical sites. It was originally developed to represent chemisorption on a set of distinct, localised adsorption sites. The linear form of the Langmuir isotherm equation is given as 

$$
\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}K_L} + \frac{C_e}{q_{\text{max}}}
$$

(3)

where $q_e$ (mg/g) is the adsorption capacity at equilibrium, $C_e$ (mg/L) is the equilibrium concentration of mercury ions, and $q_{\text{max}}$ (mg/g) and $K_L$ (L/mg) are the Langmuir constants related to the maximum adsorption capacity and energy of adsorption, respectively. The values of $q_{\text{max}}$ and $K_L$ were determined from the slope and intercept, respectively, of the linear plot of $C_e/q_e$ vs. $C_e$, and are given in Table 1.

The favourability of the adsorption process was indicated by the dimensionless equilibrium parameter $R_L$, which was calculated from the following equation [40]:

$$
R_L = \frac{1}{1 + K_L C_0}
$$

(4)

The parameter $R_L$ indicates the isotherm to be either unfavourable ($R_L > 1$), linear ($R_L = 1$), favourable ($0 < R_L < 1$), or irreversible ($R_L = 0$). In this work, the values of $R_L$ were between 0.476 and 0.0430 at 30 °C. These values confirmed the ongoing adsorption of mercury using modified palm shell activated carbon, which confirms that the Langmuir isotherm model was favourable for this study.

The Freundlich isotherm model is applicable to highly heterogeneous surfaces, and an adsorption isotherm lacking a plateau indicates a multi-layer adsorption. The linear form of the Freundlich isotherm is given by the following equation [41]:

$$
\log q_e = \log K_F + \frac{1}{n} \log C_e
$$

(5)

where $q_e$ is the amount of adsorbate adsorbed per gram of modified activated carbon at equilibrium (mg/g), $C_e$ is the equilibrium concentration of the adsorbate (mg/L), and $K_F$ and $1/n$ are Freundlich constants that represent the adsorption capacity and the intensity of adsorption, respectively. The values of $K_F$ and $1/n$ were obtained from the intercept and slope, respectively, of the plot of $\log q_e$ vs. $\log C_e$, and are given in Table 1. A $1/n$ value of less than one indicates a normal Langmuir isotherm, whereas a $1/n$ value of greater than one is indicative of cooperative adsorption. In this study, the $1/n$ values were between 0.63 and 0.57, which again indicated a normal Langmuir isotherm.

Another popular equation for the analysis of isotherm is that proposed by Dubinin and Radushkevich [42].

$$
\ln q_e = \ln q_{\text{max}} - B \varepsilon^2
$$

(6)

where $q_e$ is D–R isotherm constant related to adsorption capacity (mg/g), $B$ is the activity coefficient related to mean free energy $E$ (kJ/mol) of adsorption per molecule of the adsorbate and can be calculated using the relationship $E = 1/(2B)^{1/2}$, and $\varepsilon$ is the Polanyi potential, and can be correlated:

$$
\varepsilon = RT \ln \left[ 1 + \frac{1}{C_e} \right]
$$

(7)

The slope of the plot of $\ln q_e$ vs. $1/\varepsilon^2$ gives $B$ and the intercept yield $q_{\text{max}}$.

Table 1.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>Langmuir isotherm parameters</th>
<th>Freundlich isotherm parameters</th>
<th>Dubinin–Radushkevich isotherm parameters</th>
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<td></td>
<td>$q_{\text{max}}$</td>
<td>$K_L$</td>
<td>$R^2$</td>
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</tr>
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<td>83.33</td>
<td>0.125</td>
<td>0.991</td>
</tr>
</tbody>
</table>

3.5. Adsorption kinetics

To study the mechanism of the adsorption process steps, such as the mass transport and chemical reaction processes, kinetic models were used to test the experimental data. The kinetics of Hg(II) adsorption on the modified palm shell activated carbon were analysed using pseudo-first-order [44], pseudo-second-order [45] and intraparticle diffusion models [46].

The pseudo-first-order kinetic model is expressed as follows:

$$
\ln(q_e - q_t) = \ln q_{\text{max}} - k_1 t
$$

(8)

where $q_e$ (mg/g) and $q_t$ (mg/g) are the amounts of the mercury(II) ions adsorbed at equilibrium and at time $t$ (min), respectively, and $k_1$ (min$^{-1}$) is the rate constant; the values were calculated from the slope of the plots of $\ln(q_e - q_t)$ vs. $t$, as given in Table 2.

The pseudo-second-order kinetic model is expressed as follows:

$$
\frac{t}{q_t} = \frac{1}{k_2 q_{\text{max}}^2} + \frac{t}{q_{\text{max}}}
$$

(9)

where $q_e$ (mg/g) and $q_t$ (mg/g) are the amounts adsorbed at equilibrium and at any time $t$ (min) and $k_2$ is the rate constant of the pseudo-second-order reaction. The values of the pseudo-second-order rate constant $k_2$ (g mg$^{-1}$ min$^{-1}$) and the adsorption capacity at equilibrium $q_{\text{max}}$ were determined from the slope and intercept, respectively, of the plot of $t/q_t$ vs. $t$ and are given in Table 2.

According to Weber and Morris [46], an intraparticle diffusion coefficient $k_{id}$ (mg/g h$^{1/2}$) is given by the equation:

$$
q_t = k_{id} t^{1/2}
$$

(10)
The intraparticle diffusion rate constant was obtained from the slope of the plot of $q_t$ vs. $t^{1/2}$ for the intraparticle diffusion model (Table 2). However the correlation coefficient is not satisfactory. The intraparticle equation did not provide a good fit to the experimental data. These results confirm the chemisorption of the adsorption process.

Table 2 summarises the values of the corresponding model parameters. The degrees of goodness of the linear plots of these kinetic models were determined by the correlation coefficients of the plots, which can also be regarded as a criterion in the determination of the efficiency of the kinetics model. The correlation coefficients for the pseudo-second-order kinetics model are greater than the correlation coefficients for the pseudo-first-order kinetics and the intraparticle diffusion models. These indicate that the adsorption system is probably best described by the pseudo-second-order kinetics model. Moreover, the calculated adsorption capacities determined using pseudo-second-order plots are in good agreement with the experimental values. This fact confirms the earlier hypothesis that the adsorption process is controlled by chemisorption.

The decrease in the $k_2$ values with increased initial metal ion concentrations is a common phenomenon observed with a variety of adsorbents used for the adsorption of Hg(II). Numerous factors can contribute to this initial concentration effect on the rate of adsorption. An increase in the metal concentration in solution appears to reduce the diffusion of metal ions in the boundary layer and to enhance diffusion in the solid. A second possible cause is the progressive decrease in covalent interactions relative to electrostatic interactions of the sites with a lower affinity for Hg$^{2+}$ with an increase in the initial Hg(II) concentration.

**3.6. Effect of temperature and the thermodynamic parameters of adsorption**

Temperature is an important factor that affects the adsorption process. In this work, the effect of the temperature on the removal efficiency of mercury from aqueous solutions using modified palm shell activated carbon was studied at different temperatures in the range of 20–35 °C. Fig. 5 shows an increasing trend in mercury removal with an increase in temperature from 20 to 35 °C, which indicate the process to be endothermic. The increase in mercury removal with an increase in temperature may be due to the increased chemical interactions between mercury ions and the functional groups on the surface of the activated carbon surface, which indicates the process to be chemisorption.

The temperature dependence of adsorption is associated with various thermodynamic parameters. To study the thermodynamics of adsorption, adsorption studies were performed at 20, 25, 30, and 35 °C.

Thermodynamic parameters, including the standard enthalpy change ($\Delta H^\circ$) (kJ/mol) and the standard entropy change ($\Delta S^\circ$) (J/K mol), were obtained using the van’t Hoff equation [47]:

$$
\Delta G^\circ = RT \ln K_L
$$

(12)

The values of $\Delta H^\circ$ and $\Delta S^\circ$ were obtained from the slope and intercept, respectively, of the plot of $\ln K_L$ vs. $1/T$, as shown in Fig. 6. The thermodynamic values of $\Delta H^\circ$, $\Delta S^\circ$ and $\Delta G^\circ$ obtained for the adsorption process of Hg(II) on activated carbon are summarised in Table 3. The enthalpy change is related to the chemical bonding; therefore, the positive value of the enthalpy of adsorption $\Delta H^\circ$ obtained in this study confirms the endothermic nature of the adsorption process, and the high value of $\Delta H^\circ$ indicates that the adsorption process is likely due to chemisorptions and strong interactions between the Hg(II) ions and the functional groups on the surface of the activated carbon. The value of $\Delta S^\circ$ is related to the ordering or the geometry of the adsorbed ions. The positive value of $\Delta S^\circ$ suggests an increase in disorder and randomness at the solid solution interface during the adsorption process. The standard Gibbs free energy change ($\Delta G^\circ$) is the fundamental criterion of spontaneity of an adsorption process. The negative values for $\Delta G^\circ$ indicate that the adsorption process is spontaneous and thermodynamically favourable. The high negative values of $\Delta G^\circ$ indicate a greater order of reaction and a stronger driving force for the adsorption of Hg(II) on the surface of the activated carbon.

<table>
<thead>
<tr>
<th>$C_0$ (mg/L)</th>
<th>$q_e$ experimental</th>
<th>Pseudo-first-order parameters</th>
<th>Pseudo-second-order parameters</th>
<th>Intraparticle diffusion value</th>
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<td>$q_t$, calculated</td>
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<td>$R^2$</td>
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<td>0.98</td>
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<td>0.98</td>
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<td>29.85</td>
<td>0.011</td>
<td>0.98</td>
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Fig. 5. Effect of temperature on the adsorption of Hg(II) on modified palm shell activated carbon (experimental conditions: adsorbent 0.1 g/50 mL, Hg(II) initial concentration of 80 mg/L, pH 8 and orbital shaking at 180 rpm).
3.7. Adsorption activation energy

The activation energy of adsorption ($E_a$) is the free energy required for the adsorption of metal ions onto activated carbon. The type of adsorption can be determined from the value of the activation energy, where a low activation energy (less than 4 kJ/mol) is characteristic of physical adsorption, and a higher activation energy (between 8 and 80 kJ/mol) suggests chemical adsorption. The activation energy for the adsorption of metal ions was calculated using the linear form of the Arrhenius equation [48]:

$$
\ln k_2 = -\frac{E_a}{RT} + \ln K_0
$$

where $K_0$ (g/mol min) is the temperature independent factor, $E_a$ (kJ mol$^{-1}$) is the activation energy of the reaction of adsorption, $R$ is the gas constant (8.314 J/mol K), and $T$ is the absolute temperature. The activation energy $E_a$ was determined from the slope of the plot of $\ln k_2$ vs. $1/T$, as shown in Fig. 7. In our study, the high value of the activation energy (68.21 kJ/mol) indicates that the adsorption process involves some chemical forces and occurs by a chemisorption process.

### Table 3

<table>
<thead>
<tr>
<th>$T$ (K)</th>
<th>$\Delta H$ (kJ/mol)</th>
<th>$\Delta S$ (J/K mol)</th>
<th>$\Delta G$ (kJ/mol)</th>
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### Fig. 6

Thermodynamic plot for the adsorption of mercury ions on modified palm shell activated carbon.

### Fig. 7

The activation energy plot for Hg(II) adsorption on modified palm shell activated carbon (experimental conditions: adsorbent 0.1 g/50 mL, Hg(II) initial concentration of 80 mg/L, pH 8 and orbital shaking at 180 rpm).

### Fig. 8

SEM micrographs of the palm shell activated carbon that was (a) virgin, (b) impregnated with TOMATS and prior to adsorption of Hg(II), or (c) impregnated with TOMATS after adsorption of Hg(II).

3.8. Scanning electron microscopy studies

Scanning electron microscopy (SEM) results were used to determine and compare the surface morphological features of the pure and palm shell activated carbon impregnated with TOMATS before and after Hg(II) adsorption. As shown in Fig. 8, the SEM micrographs of the native, modified and mercury-adsorbed palm shell activated carbon differ. The surface of pure palm shell activated carbon (Fig. 8a) exhibits porous properties, smooth surfaces with long linear ridges and rough surfaces with oval ridges and micropores. In contrast, the palm shell activated carbon impregnated with
TOMATS exhibits a uniform and narrow range of pore sizes (Fig. 8b). When the virgin palm shell activated carbon was modified, the pore surface was coated with TOMATS, and a significant change was observed in the surface properties. Significant differences in the surface structure of the impregnated palm shell activated carbon and the surface after adsorption of Hg(II) were observed. SEM photographs obtained at the same magnifications indicate significant improvement in the microstructure of the adsorbent. The morphology changed after the TOMATS was bound with Hg(II). Aggregates of white needles were observed on the surface (Fig. 8c), which were presumed to be complexes formed between the TOMATS and Hg$^{2+}$ ions.

3.9. Energy-dispersive X-ray analysis (EDAX)

EDAX analysis was employed to confirm the presence of TOMATS and mercury on the surface of PSAC. The corresponding EDAX spectrum and the composition table are shown in Fig. 9. From Fig. 9a, in the case of virgin palm shell activated carbon, the characteristic peaks of nitrogen and sulphur were not observed, whereas they were observed in Fig. 9b. This result indicates that TOMATS was impregnated at the PSAC. Based on Fig. 9c, a significant amount of mercury is present in the sample and is uniformly distributed, whereas in Fig. 9d, the amount of mercury is less than that in Fig. 9c. The results show that mercury becomes the principal element of the modified palm shell activated carbon surface. This was due to the fact that mercury ions were chemisorbed on the surface of modified palm shell activated carbon, whereas the mercury ions were physisorbed on the surface of the virgin palm shell activated carbon. Therefore, EDAX analysis provides direct evidence for the specific adsorption of mercury ions onto the surface of modified palm shell activated carbon.

3.10. Surface area and pore size analysis

Nitrogen adsorption–desorption isotherms were recorded for the virgin and grafted palm shell activated carbon. The specific surface area obtained according to the Brunauer–Emmett–Teller (BET) model of virgin palm shell activated carbon was 636.1633 m$^2$/g at 77 K, using N$_2$ as adsorbate. The specific surface area decreased upon impregnation with the task specific ionic liquid (TOMATS). This due to filling the pores of the palm shell activated carbon surfaces with active TOMATS functional groups.

Table 4 summarises the pore properties of the virgin and modified palm shell activated carbon samples.

![Table 4](https://example.com/table4.png)

<table>
<thead>
<tr>
<th>Weight of impregnated TOMATS (g/1 g PSAC)</th>
<th>Specific surface area (m$^2$/g)</th>
<th>Pore diameter (nm)</th>
<th>Total pore volume (cm$^3$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00$^a$</td>
<td>636.1633</td>
<td>1.84500</td>
<td>0.293430</td>
</tr>
<tr>
<td>0.05</td>
<td>513.0892</td>
<td>2.15855</td>
<td>0.276882</td>
</tr>
<tr>
<td>0.1</td>
<td>364.5499</td>
<td>1.82947</td>
<td>0.166733</td>
</tr>
<tr>
<td>0.2</td>
<td>275.9430</td>
<td>2.24339</td>
<td>0.154762</td>
</tr>
<tr>
<td>0.3</td>
<td>107.6917</td>
<td>2.40886</td>
<td>0.0648540</td>
</tr>
</tbody>
</table>

$^a$ Virgin palm shell activated carbon.

Fig. 9. EDAX spectrum of palm shell activated carbon: (a) Virgin palm shell activated carbon; (b) palm shell activated carbon modified with TOMATS; (c) palm shell activated carbon modified with TOMATS and adsorbed with mercury; and (d) virgin palm shell activated carbon adsorbed with mercury.

TOMATS exhibits a uniform and narrow range of pore sizes (Fig. 8b). When the virgin palm shell activated carbon was modified, the pore surface was coated with TOMATS, and a significant change was observed in the surface properties. Significant differences in the surface structure of the impregnated palm shell activated carbon and the surface after adsorption of Hg(II) were observed. SEM photographs obtained at the same magnifications indicate significant improvement in the microstructure of the adsorbent. The morphology changed after the TOMATS was bound with Hg(II). Aggregates of white needles were observed on the surface (Fig. 8c), which were presumed to be complexes formed between the TOMATS and Hg$^{2+}$ ions.
3.11. Desorption study

Modified palm shell activated carbon with adsorbed Hg(II) ions was washed with double-distilled water and subsequently dried at 100 °C. The desorption of pre-adsorbed Hg(II) ions was studied in bulk solution (1.0 × 10^{-5} M). It was observed that no appreciable activity of adsorbed species was transferred from adsorbent surface to the desorptive solution. These results show that the process of adsorption is almost irreversible and chemisorptive in nature.

3.12. Comparison of the removal efficiency between this and previously reported works

The maximum mercury ion removal capacities using modified palm shell activated carbon were compared with various adsorbents reported in the literature [26,47,49–51] (Table 5). The differences in adsorption capacities shown by the modified palm shell activated carbon and other adsorbents are due to each adsorbent containing different types of functional groups. The removal efficiency values obtained in this work appear better than those obtained using other adsorbents.

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References


| Table 5 | Adsorption capacity of various adsorbents as reported in the literature. |
| --- | --- | --- | --- | --- |
| Adsorbent | Maximum adsorption capacity | Optimum pH | Maximum concentration C₀ | References |
| Manganese dioxide nanowhiskers | 199.51 mg/g | 6–9 | 40 mg/L | [26] |
| Extracellular biopolymer poly(γ-glutamic acid) | 77.57–96.79 mg/g | 4–6 | – | [47] |
| Mercapto-functionallized core–shell structured nano-magnetic Fe₃O₄ polymers | 129.9–256.4 mg/g | – | – | [49] |
| Carbonised sugi wood | 48.5 mg/g | 6 | 100 mg/L | [50] |
| Activated carbons | 73.5–151.3 mg/kg | 5 | 120 mg/L | [51] |
| Modified palm shell activated carbon | 83.33 mg/g | 6–8 | 200 mg/L | This work |
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