ABSTRACT

The surface modification of ground tyre rubber (GTR) containing hydroxyl groups was carried out by atom transfer radical polymerization using a two-step reaction procedure. The process consisted of immobilization of an ATRP initiator such as 2-bromoisoamyl bromide and controllable radical polymerization of maleic anhydride (MAH). The resulting GTR-g-MAH was characterized by Fourier transform infrared spectroscopy and X-ray photoelectron spectroscopy. The results demonstrated that the graft yield of new polymer could reach 69.4% on GTR surface. Then the grafted GTR was used as an adsorbent for removal of lead ions from aqueous solution. It was observed that factors such as solution pH, contact time, initial lead concentration and graft yield exerted considerable influence on lead adsorption capacity of GTR-g-MAH. The adsorption process indicated that the pseudo-second-order kinetic model fitted the experimental data well, and the equilibrium of adsorption could be described by Freundlich isotherm model. The maximum adsorption capacity of GTR-g-MAH calculated from Langmuir isotherm reached 144 mg.g⁻¹. It was found that the GTR-g-MAH particles had significantly greater adsorption capacity and faster adsorption kinetics for lead adsorption than unmodified GTR particles.

INTRODUCTION

As cross-linked and non-biodegradable materials, much of waste rubber from rejected tyres and other rubber materials on the one hand are discarded and dumped improperly, which imposes serious threats on the public health and safety as well as environment, and on the other hand, it causes the loss of natural resources. To eliminate those adverse situations and reduce the production cost of rubber, many efforts are being made to reuse and recycle waste rubbers. A potential solution of disposal rubber involves grinding which converts it into granulates and powders often called ground tyre rubber (GTR) and using them as filler to blend with fresh rubbers [1] or toughening agent for thermoplastics [2-4], etc.. However, incorporation of GTR into polymer matrices significantly impairs the mechanical properties and processability of resulting materials which because of poor interfacial adhesion and
lack of reactive sites on GTR surface \[1,4\], obstructs effective utilization of GTR particles in polymer composites. Thus surface modification was proposed to improve the interfacial compatibility between GTR and the substrates.

It has been reported that there are various kinds of functional groups [4-6], such as double bond, carboxyl, keto, hydroxyl groups on the GTR surface which can be used for further GTR derivatization to modify some of their specific surface properties. A cheap waste material such as GTR has been extensively studied as an adsorbent for removal of heavy metal ions from water or wastewater [7-9] due to their reactive groups, porous structure as well as chemical additives (i.e., ZnO, carbon and sulphur) [7,9]. Because of the known good removal efficiency for some heavy metals, GTR grafted with reactive monomers, such as maleic anhydride and acrylamide can produce excellent results in metal removal, especially lead ions, though the removal efficiency of lead on pristine GTR is lower than that of Hg(II) and Cd(II) due to different adsorption mechanisms [7-9].

Lead, a cumulative poison, is widely used as an intermediate in processing industries such as electroplating, paint and dyes, explosive manufacturing and lead batteries [10]. It is well known that the presence of lead ion in water even at a very low level (5 ng.mL\(^{-1}\)) would be harmful to aquatic life and endanger human health because of its toxicological, potential carcinogenic and neurological effects [11]. Therefore, it is essential to use surface modification techniques to enhance lead adsorption capacity of GTR through introduction of reactive groups so that these GTR particles can be effectively used as an adsorbent or ion exchanger.

Several techniques, including both chemical and physical processes, have been developed to enhance removal capacity of adsorbents on heavy metals [12-15]. Among them, surface graft polymerization is attractive because it can provide materials with tailored properties for practical application by easy and controllable introduction of grafted chains while it has minor influence on bulk properties of grafted adsorbent. In particular, atom transfer radical polymerization (ATRP) has been proven to be versatile especially for polymerization of some vinyl monomers, such as styrene, methyl methacrylate and acrylate [16]. By immobilizing a suitable ATRP initiator on matrix surface, monomer can be initiated and propagated from matrix surface to form polymer bushes. As a surface modification technique, this method has been used to graft some vinyl monomers successfully on silicon wafers [17], GTR particles [18], chitosan beads [19] and PU membranes [20]. Although it has been reported that GTR particles can be functionalized by grafting styrene and acrylate via ATRP method [18], there are still no reports on grafting MAH on GTR via ATRP and its subsequent metal adsorption on MAH modified GTR.

The aim of this work is to improve adsorption capacity of GTR particles by grafting MAH on its surface to adsorb lead ions and to illustrate adsorption processes and evaluate the feasibility of applying modified GTR as an adsorbent and ion exchanger in practical heavy-metal removal. The influence of different parameters on lead uptake, such as pH value, initial concentration, contact time and graft yield was investigated in batch conditions. Furthermore, this study may also provide insight into lead ions adsorption from aqueous solution in terms of equilibrium and kinetics.

**EXPERIMENTAL**

**Materials**

Ground tyre rubber (GTR) with a maximum diameter of 125 \(\mu\)m (120 mesh) was supplied by Daziran Fine Rubber Powder Mill, Hejiang, Sichuan, China. The original GTR was extracted (Soxhlet extraction) with acetone to remove major part of the plasticizer and additives incorporated in rubber processing, and it was dried in a vacuum oven until reaching constant weight. CuBr (99% purity) was purified by rinsing with ice acetic acid and ethanol repeatedly under N\(_2\) atmosphere and then dried in a vacuum oven. Triethylamine (Et\(_3\)N) was purified by refluxing over KOH and distilled under N\(_2\) atmosphere. Tetrahydrofuran (THF) and \(N,N\)-dimethylformamide (DMF) were purified according to standard procedure. Other chemicals, such as maleic anhydride (MAH), 2-bromoisobutryl bromide (BIBB), bipyridyl (bipy) and lead(II) acetate
trihydrate, were analytical grades and used without further purification.

**Immobilization of ATRP Initiator onto GTR Surface**

About 1 g of treated GTR was added into a 100-mL flask containing 25 mL of THF and 5 mL of Et₃N. After degassing and backfilling with N₂ for three cycles, the solution was gently stirred in an ice bath. One millilitre of BIBB was then added into the solution dropwise under N₂ atmosphere, and the solution was refluxed in an oil bath under stirring for about 8 h. The brominated GTR was filtered and washed with ethanol and deionized water repeatedly, and then dried in a vacuum oven at 60°C for 12 h.

**Surface-initiated Polymerization of MAH via ATRP Method**

Surface-initiated polymerization of MAH onto GTR was carried out in the presence of CuBr/bipy catalytic system with the molar ratio of monomer/CuBr/bipy in 100:1:2. Thus in a typical operation, a solution containing 5 mL of DMF, 43.05 mg (0.3 mmol) CuBr, 93.6 mg (0.6 mmol) bipy and 2.94 g (30 mmol) MAH was stirred for 5 min under N₂ bubbling until the monomer was completely dissolved in the solution. Then, 0.5 g of brominated GTR was slowly added into solution in N₂ atmosphere. The content, introduced in a flask, was deoxygenated via three cycles of freezing, degassing and thawing and then it was sealed in dry nitrogen. The reaction was allowed to proceed at 110°C in an oil bath for about predetermined duration. The resulting product designated as GTR-g-MAH was separated and washed with acetone and deionized water repeatedly to remove any impurities, and then dried in a vacuum oven at 65°C for 12 h.

The graft yield of MAH on GTR was calculated with the following equation:

\[
\text{Graft yield (\%) = } \left( \frac{W_0 - W_1}{W_0} \right) \times 100\%
\]  

(1)

where \( W_0 \) is the initial weight of original GTR after extracted with acetone and \( W_1 \) is the weight of treated GTR-g-MAH.

**Adsorption of Lead with GTR-g-MAH and Unmodified GTR**

Lead(II) solutions with desired concentrations were prepared from lead(II) acetate trihydrate and deionized water. Approximately 0.1 g of GTR-g-MAH (polymerization time of 40 h) and of GTR were each added separately into a 150 mL of lead stock solution. The flasks were sealed and shaken at 150 rpm in a constant temperature shaker at 25°C for a desired duration, and were then taken out at a desired time interval. Finally, the concentration of lead in each solution was determined using a Varian SpectrAA 220FS atomic adsorption spectrometer. All the experiments were carried out in duplicates and the average values were used for further calculations.

The adsorbed amounts of lead per weight of samples at time \( t \), \( q_t = (\text{mg.g}^{-1}) \), were calculated from the mass balance equation as:

\[
q_t = \frac{(C_0 - C_t)V}{m}
\]

(2)

where \( C_0 \) (mg.L⁻¹) and \( C_t \) (mg.L⁻¹) represent the initial lead concentration and the lead concentrations at a given time \( t \) (min), respectively, \( V \) (mL) is the volume of the solution and \( m \) (g) is the weight of GTR added into each flask.

**Characterizations**

FTIR spectra were obtained on a Perkin-Elmer FT-IR 9000 spectrometer. X-ray photoelectron spectrometer (XPS) analysis was performed on a Kratos XSAM 8000 spectrometer using a monochromatized AlKα X-ray radiation. All the binding energies (BEs) were referenced to the C₁s hydrocarbon peak at 284.8 eV.

**RESULTS AND DISCUSSION**

**Surface Modification of GTR Particles**

**Determination of Hydroxyl Group Content and Graft Yield on GTR Surface**

The absorption peaks in FTIR spectrum (Figure 1a) of GTR at 3420 cm⁻¹ (\( \nu_{\text{O-H}} \)) and 1140 cm⁻¹ (\( \nu_{\text{C-O}} \)) show that there are hydroxyl groups on the GTR surface, and the content of hydroxyl could be determined by an indirect chemical titration based on the following equation:

\[
W_0 - W_1 \propto W_{\text{OH}}
\]

where \( W_{\text{OH}} \) is the weight of hydroxyl groups.

**Adsorption Amounts (mg.g⁻¹)**

The adsorption capacities of lead ions in GTR-g-MAH and unmodified GTR particles are given in Table 1. As seen, adsorption capacities of GTR-g-MAH particles are higher than those of unmodified GTR particles for a wide range of lead concentrations, indicating that GTR-g-MAH samples are more effective than unmodified GTR samples in adsorbing lead ions at different concentrations.

**Characteristics**

FTIR spectra were obtained on a Perkin-Elmer FT-IR 9000 spectrometer. X-ray photoelectron spectrometer (XPS) analysis was performed on a Kratos XSAM 8000 spectrometer using a monochromatized AlKα X-ray radiation. All the binding energies (BEs) were referenced to the C₁s hydrocarbon peak at 284.8 eV.

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**Surface Modification of GTR Particles**

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\[
W_0 - W_1 \propto W_{\text{OH}}
\]

where \( W_{\text{OH}} \) is the weight of hydroxyl groups.
FTIR Spectroscopy

Figure 1 shows the FTIR spectra of GTR after BIBB immobilization and MAH grafting. The absorption peaks of original GTR (Figure 1a) at 3420 cm$^{-1}$ and 1140 cm$^{-1}$ are assigned to the stretching vibration of O-H and C-O bonds, respectively, which support the interaction of initiator with hydroxyl group on GTR surface to form surface-immobilized initiator [18,19], as indicated in Scheme I. The absorption band at 1635 cm$^{-1}$ is attributed to the C=C vibration mode, which coincides with the report that there is a double bond on the surface of GTR and can also be used to perform modification of GTR [6]. In comparison with Figure 1a, Figure 1b shows the presence of obvious absorptions at 565 cm$^{-1}$ (νC-Br) and 1742 cm$^{-1}$ (νC=O) suggesting the initiator was successfully anchored onto GTR surface.

Figure 1c demonstrates that the new polymer was formed on the surface of GTR particles which is indicated by the appearance of a new peak at 1725 cm$^{-1}$, the characteristic absorption band of carbonyl group. The absence of absorption peak above 1770 cm$^{-1}$ for anhydride implies that the anhydride was eliminated due to its hydrolysis in presence of water or alcohol. The absorptions at 2925 cm$^{-1}$ and 2850 cm$^{-1}$ for stretching vibration of C-H bond show greater intensity, which also indicates the incorporation of MAH onto the GTR surface. The postulation can also be testified by the
Figure 2. XPS wide scan spectra of the GTR surface after (a) immobilization of ATRP initiator BIBB and (b) subsequent ATRP polymerization of MAH.

peak shift of C-O vibration from 1140 cm⁻¹ to 1160 cm⁻¹ (Figure 1) resulted from the change of chemical environment after graft polymerization. Other absorption bands do not change dramatically after modification, which implies that surface-initiated ATRP is a promising technique for chemical modification without bulk damage of grafted GTR particles. However, there are also other ways to graft MAH onto rubber particles, such as chemical initiation [21], melt grafting [22] and radiation-induced graft polymerization [23], which either damage the bulk properties or cannot produce high graft yields in comparison with ATRP graft polymerization.

XPS Analysis
The XPS wide spectra of brominated and grafted GTR samples are illustrated in Figure 2. For brominated GTR, the Si, Ca and Zn are clearly observed from the XPS wide spectrum (Figure 2a), which originate from the SiO₂, CaCO₃ and ZnO used in rubber production process. The absence of Br signal in brominated GTR is possibly due to its low content and low sensitivity. Compared with Figures 2a and 2b, the component and content of elements change dramatically after graft polymerization. The surface C₁s content decreases from 86.6% to 85.7% due to the formation of MAH copolymer layer. The presence of MAH brushes on GTR surface can also be inferred to increased O₁s content from 9.1% to 13.7% and reduced measured Si₂p content from 1.2% to 0.6% as well as the disappearance of Zn (2.5%) and Ca (0.5%) signals.

In order to investigate chemical structure in detail, the XPS spectra of C₁s core level region for two samples are shown in Figure 3. The C₁s core level region also indicates the formation of polymeric layers (Figure 3b) from the appearance of a new peak at 289.7 eV (4.2%) attributed to carboxylic carbon of -COOH. Owing to the contribution of polymeric brushes, the component at 284.6 eV assigned to C-C/C-H aliphatic hydrocarbon significantly decreases from 81% to 73.6%, while the C-O component at 286.3 eV increases from 19% to 22.2%, indicating the high polymer thickness after graft polymerization.

The FTIR and XPS results confirmed that the MAH was successfully grafted onto GTR surface by surface-initiated ATRP polymerization. Furthermore, the modified GTR particles as adsorbents were utilized to remove lead ions from aqueous solution.

Lead Adsorption on GTR-g-MAH and Unmodified GTR
Effect of Initial pH Value on Lead Adsorption
It is known that the pH of a solution is the most
important factor affecting metal adsorption on the adsorbent [24-27]. In this work, the effect of pH on lead adsorption is shown in Figure 4. As indicated in this figure, the equilibrium adsorption quantity of Pb(II) on two adsorbents significantly increases with increased pH from 4 to 5, whereas there is a minor influence on lead adsorption capacity for pH less than 4. With a further increase in pH from 5 to 7 for GTR-g-MAH, however, the equilibrium adsorption capacity decreases slightly. In contrast, the equilibrium adsorption capacity of GTR is maintained at about the same level at pH from 5 to 7. For the system with pH beyond 7 adsorption was not determined because the formation of Pb(OH)\(^+\) and Pb\(^{2+}\) ions [27]. Consequently, these variations related to solution pH considerably enhance electrostatic interaction between lead ions and the adsorbent and thus increase adsorption capacity of GTR-g-MAH. In conclusion, pH 5 was selected as an optimum value for conducting further adsorption experiments according to influence of solution pH on lead adsorption.

Effect of Contact Time and Initial Concentration

Figure 5 shows the effect of contact time on the adsorbed amount of Pb(II) by GTR-g-MAH and GTR from solutions at different initial concentrations of Pb(II). In case of GTR-g-MAH the lead adsorption capacity increases sharply with increase of contact time in the initial 40 min and attains equilibrium
within 80 min, while in case of GTR, equilibrium adsorption is established within 120 min. It is also clear from Figure 5 that adsorption capacity increases with the increase in initial lead concentration. The equilibrium adsorbed amounts of Pb(II) are found to increase from 29.2 to 69.3 mg.g\(^{-1}\) and 9.6 to 22.5 mg.g\(^{-1}\) for GTR-g-MAH and GTR when the initial concentrations increase from 50 to 100 mg.L\(^{-1}\), respectively. The above results show that the amount of Pb(II) adsorbed by GTR-g-MAH is much greater than that adsorbed by GTR especially in high initial lead concentration. The adsorption rate of Pb(II) on GTR-g-MAH is more rapid than that on unmodified GTR, which is perhaps due to the higher content of surface functional groups on the former adsorbent after grafting modification. The higher adsorption capacity and adsorption rate indicate that GTR-g-MAH is suitable to treat wastewater containing Pb(II) ions.

**Effect of Graft Yield on Lead Adsorption Capacity**

The effect of graft yield for various polymerization times on adsorption capacity is shown in Table 2. As it is evident from this table, adsorption capacity increases considerably with the increased graft yield within polymerization time below 30 h, and then increases slightly with a further increase in polymerization time due to a small increased graft yield. The graft yield significantly influences lead adsorption capacity because the content of MAH grafted onto GTR determines the quantity of adsorption sites on GTR surface which can chemically bind to lead ions. The more adsorption sites, the greater adsorption capacity. Therefore, with the increased polymerization time, the surface of GTR is increasingly covered by MAH brushes, and thus there are more adsorption sites available for GTR particles to improve the adsorption capacity on lead ions.

**Adsorption Kinetics**

In order to investigate the controlling mechanism of adsorption processes such as mass transfer and chemical reaction, some liquid-phase adsorption kinetic models were put forward to describe adsorption kinetic process [28]. Here the kinetic data were analyzed using Lagergren pseudo-first-order and pseudo-second-order kinetic models expressed as:

\[
\frac{dq_t}{dt} = k_1(q_e - q_t)
\]

\[
\frac{dq_t}{dt} = k_2(q_e - q_t)^2
\]

where \(q_t\) (mg.g\(^{-1}\)) and \(q_e\) (mg.g\(^{-1}\)) are the amounts adsorbed per unit mass of adsorbent at any time and at equilibrium, respectively, \(k_1\) (min\(^{-1}\)) and \(k_2\) (g.mg\(^{-1}\).min\(^{-1}\)) are the rate constants of Lagergren and pseudo-second-order model, respectively. Integrating eqns (3) and (4) using \(q_t(0) = 0\) and \(q_t(t) = q_e\), the equations become:

\[
\ln(q_e - q_t) = \ln(q_e) - k_1t
\]

\[
\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}
\]

The plots of ln(q\(_e\)-q\(_t\)) and t/q\(_t\) versus t should be straight lines, thus \(q_e\), \(k_1\) and \(k_2\) can be obtained from their slopes and intercepts of the curves.

Based on eqns (5) and (6), the values of parameters and correlation coefficient (r) are listed in Table 3, and the two kinetic models for GTR-g-MAH are illustrated in Figure 6. It is observed that the values of correlation coefficient obtained from pseudo-second-order kinetic model for both GTR and GTR-g-MAH are higher than those obtained from

<table>
<thead>
<tr>
<th>Polymerization time (h)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graft yield (%)</td>
<td>32.5</td>
<td>48.6</td>
<td>61.3</td>
<td>69.4</td>
</tr>
<tr>
<td>Adsorption capacity (mg.g(^{-1}))</td>
<td>48.1 (1.1)</td>
<td>60.7 (1.1)</td>
<td>71.2 (1.2)</td>
<td>76.8 (1.1)</td>
</tr>
</tbody>
</table>

Values in parentheses calculated from three samples are standard deviations.
Lagergren pseudo-first-order. Moreover, the values of adsorption capacity at equilibrium (qe) estimated from pseudo-second-order for two adsorbents are close to the experimental values (qe,ex). Therefore, the pseudo-second-order model, an indication of chemisorptions mechanism, fits the experimental data better than the pseudo-first-order model.

**Adsorption Equilibrium**

Adsorption isotherm describes qualitatively the nature of the solute-surface interaction as well as the specific relation between the concentration of adsorbate and its degree of accumulation onto adsorbent surface at constant temperature. Adsorption capacity can be evaluated by the adsorption isothermal experiments and a model on adsorption parameters of lead ions by GTR and GTR-g-MAH particles can be given using Freundlich [29] and Langmuir [30] isothermal equations expressed as:

\[
q_e = \frac{K_F C_e^{1/n}}{1 + K_F C_e}
\]  
(7)

\[
q_e = \frac{q_m K_L C_e}{1 + K_L C_e}
\]  
(8)

or in the linear form as:

\[
\ln q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e
\]  
(9)

\[
\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}
\]  
(10)

where C_e (mg.L⁻¹) is the liquid phase concentration of metal at equilibrium; K_F (mg.g⁻¹) and 1/n are the Freundlich adsorption coefficient and exponent related to adsorption capacity and energy of adsorption, respectively, q_m (mg.g⁻¹) and K_L (L.mg⁻¹) are the Langmuir constants related to the maximum metal adsorption capacity and the heat of adsorption, respectively.

The corresponding constants and the correlation coefficient (r) obtained from the linear form of eqns (9) and (10) are presented in Table 4, and two adsorption isothermal models for GTR-g-MAH are illustrated in Figure 7. The results indicate that Freundlich isotherm is more capable to fit the experimental data over the experimental range studied compared to Langmuir isotherm, since the Freundlich presents greater correlation coefficient. As shown

Table 3. Parameters of two kinetic models for lead adsorption on both GTR and GTR-g-MAH (V: 150 mL; C_0: 100 mg.L⁻¹; adsorbent dose: 0.1 g; T: 25°C; agitation rate: 150 rpm; initial pH: 5.0).

<table>
<thead>
<tr>
<th>Kinetic models</th>
<th>Parameters</th>
<th>GTR</th>
<th>GTR-g-MAH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>q_e (mg.g⁻¹)</td>
<td>24.4 (0.8)</td>
<td>84.8 (1.3)</td>
</tr>
<tr>
<td></td>
<td>k_1 (min⁻¹)</td>
<td>0.0115 (0.0018)</td>
<td>0.0248 (0.0034)</td>
</tr>
<tr>
<td>Laggren pseudo-first-order</td>
<td>r</td>
<td>0.9796</td>
<td>0.9599</td>
</tr>
<tr>
<td></td>
<td>q_e,ex (mg.g⁻¹)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>k_2 (g.mg⁻¹.min⁻¹)</td>
<td>33.7 (0.7)</td>
<td>81.2 (1.3)</td>
</tr>
<tr>
<td>Pseudo-second-order</td>
<td>r</td>
<td>0.0015 (0.0003)</td>
<td>0.0031 (0.0005)</td>
</tr>
<tr>
<td></td>
<td>-</td>
<td>29.6 (0.9)</td>
<td>76.8 (1.1)</td>
</tr>
</tbody>
</table>

Values in parentheses calculated from four samples are standard deviations.
Table 4. Freundlich and Langmuir isotherm parameters for lead adsorption on GTR and GTR-g-MAH (V: 150 mL; range of initial concentration: 20-200 mg.L⁻¹; adsorbent dose: 0.1 g; T: 25°C; agitation rate: 150 rpm; contact time: 8 h; initial pH: 5.0).

<table>
<thead>
<tr>
<th>Type of isotherm</th>
<th>Parameters</th>
<th>GTR</th>
<th>GTR-g-MAH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K_f (L.mg⁻¹)</td>
<td>2.44 (0.21)</td>
<td>5.41 (0.32)</td>
</tr>
<tr>
<td></td>
<td>1/n</td>
<td>0.5046 (0.0615)</td>
<td>0.5690 (0.0683)</td>
</tr>
<tr>
<td></td>
<td>r</td>
<td>0.9986</td>
<td>0.9999</td>
</tr>
<tr>
<td>Langmuir</td>
<td>K_L (L.mg⁻¹)</td>
<td>0.0179 (0.0027)</td>
<td>0.0622 (0.0084)</td>
</tr>
<tr>
<td></td>
<td>q_m (mg.g⁻¹)</td>
<td>42.3 (1.3)</td>
<td>144.3 (2.0)</td>
</tr>
<tr>
<td></td>
<td>r</td>
<td>0.9893</td>
<td>0.9977</td>
</tr>
</tbody>
</table>

Values in parentheses calculated from four samples are standard deviations.

Table 5. The comparison of lead uptake capacity of different adsorbents.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>q_max (mg.g⁻¹)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Palm shell-based activated carbon</td>
<td>82.4</td>
<td>[10]</td>
</tr>
<tr>
<td>Sargassum sp.</td>
<td>266.0</td>
<td>[11]</td>
</tr>
<tr>
<td>Palm shell activated carbon</td>
<td>95.2</td>
<td>[25]</td>
</tr>
<tr>
<td>S. alterniflora activated carbon</td>
<td>99.0</td>
<td>[32]</td>
</tr>
<tr>
<td>The commercial activated carbon (ST1000)</td>
<td>43.0</td>
<td>[32]</td>
</tr>
<tr>
<td>Tamarind wood activated carbon</td>
<td>43.9</td>
<td>[33]</td>
</tr>
<tr>
<td>Dead marine algae biomass</td>
<td>41-217</td>
<td>[34]</td>
</tr>
<tr>
<td>Pseudomonas aeruginosa PU21</td>
<td>70, 110</td>
<td>[35]</td>
</tr>
<tr>
<td>GTR-g-MAH</td>
<td>144.3</td>
<td>This study</td>
</tr>
</tbody>
</table>

Figure 7. The comparison of two adsorption isothermal models for lead adsorption onto GTR-g-MAH particles (V: 150 mL; range of initial concentration: 20-200 mg.L⁻¹; adsorbent dose: 0.1 g; T: 25°C; agitation rate: 150 rpm; contact time: 8 h; initial pH: 5.0).

in Figure 7, the predicted values (q_e) of Freundlich isotherm are in good agreement with those of experimental data, implying that the adsorption process involves coverage of multimolecular layers.

It is also observed from Table 4 that the values of 1/n for both GTR and GTR-g-MAH are less than 1, indicating that lead adsorption on two adsorbents is favourable [31]. Moreover the value of Freundlich adsorption coefficient, K_f, of GTR-g-MAH is higher than that of GTR, suggesting that GTR-g-MAH is more suitable for Pb(II) removal than GTR. The maximum adsorption capacity of Pb(II) on GTR-g-MAH calculated from Langmuir isotherm is 144.3 mg.g⁻¹, which is larger than that of the majority of adsorbents presented in Table 5.

CONCLUSION

GTR particles were functionalized by covering the
surface with a layer of MAH copolymer through surface-initiated ATRP polymerization to achieve enhanced removal of lead (II) ions from aqueous solution. The FTIR and XPS analyses indicated that the MAH was successfully grafted onto the GTR surface. The adsorption of lead on GTR-g-MAH was found to be greatly dependent on solution pH, and the optimal pH value for removal of lead was determined to be 5. The adsorption results showed that the GTR-g-MAH particles were fast in adsorbing lead ions and the maximum adsorption capacity on GTR-MAH was around 144 mg.g⁻¹, which is greater than that of the unmodified GTR. Pseudo-second-order model and Freundlich isotherm model were found to fit the kinetic experimental data and equilibrium data well, respectively. The results obtained above indicated that the GTR-g-MAH is an effective adsorbent for removal of lead ions.

NOTATIONS

\[ W_0 \ (g) \quad \text{Initial weight of original GTR after extracted with acetone} \]
\[ W_1 \ (g) \quad \text{The weight of treated GTR-g-MAH} \]
\[ C_0 \ (mg.L^{-1}) \quad \text{Initial concentration of lead ions} \]
\[ C_t \ (mg.L^{-1}) \quad \text{The lead concentration at a given time t (min)} \]
\[ C_e \ (mg.L^{-1}) \quad \text{The liquid phase concentration of lead ions at equilibrium} \]
\[ q_t \ (mg.g^{-1}) \quad \text{The amount of lead adsorbed per unit mass of adsorbent at any time} \]
\[ V \ (mL) \quad \text{The volume of the adsorbed solution} \]
\[ m \ (g) \quad \text{The weight of adsorbent} \]
\[ q_e \ (mg.g^{-1}) \quad \text{The amount of lead adsorbed per unit mass of adsorbent at equilibrium} \]
\[ k_1 \ (min^{-1}) \quad \text{Rate constant of Lagergren pseudo-first-order model} \]
\[ k_2 \ (g.mg^{-1}.min^{-1}) \quad \text{Rate constant of pseudo-second-order model} \]
\[ q_{e,ex} \ (mg.g^{-1}) \quad \text{Experimentally adsorbed amount at equilibrium} \]
\[ K_F \ (mg.g^{-1}) \quad \text{Freundlich adsorption coefficient related to adsorption capacity} \]
\[ 1/n \quad \text{Freundlich adsorption exponent related to energy of adsorption} \]
\[ K_L \ (L.mg^{-1}) \quad \text{Langmuir adsorption constant related to the maximum metal adsorption capacity} \]
\[ q_m \ (mg.g^{-1}) \quad \text{Langmuir adsorption constant related to the maximum metal adsorption capacity} \]
\[ r \quad \text{Correlation coefficient} \]

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