Construction of adsorptive nanorods from polyoxometalates and ionic liquid and their adsorption properties for silver ion from AMD

Huixin Zhang, Jie Zhang, Manli Cui, Xiu-hong Jin, Xu Han and Youchen Wang

ABSTRACT
A new structure of hybrid nanorods adsorbent ([n-BBIM]$_9$PW$_9$O$_{34}$) was synthesized by a simple molecular assembly of polyoxometalates with ionic liquids (ILs). The nanocomposite was characterized by Fourier transform infrared (FT-IR), ultraviolet-visible (UV-Vis), scanning electron microscope, energy dispersive X-ray and X-ray diffractometer. Adsorption of silver from acid mine drainage (AMD) was studied using batch experiments. The impact of several parameters, like ion concentration, pH, adsorbent dosage, and temperature was elucidated and optimization was carried out by single-factor experiment and response surface methodology. Analysis of variance of the quadratic model suggested that experimental data were excellently fitted to the quadratic model. Optimum conditions for removal of Ag$^{+}$ from AMD were determined to be an initial concentration 143 mg/L, adsorbent dosage 2.69 g/L, temperature 35°C to achieve the maximum adsorption of Ag$^{+}$ 99.03%, which was very close to the predicted value (100%). The adsorption was confirmed as oxidation-reduction mechanism following a complexation process, and has been verified according to results from FT-IR and UV-vis spectra. The selective experiment suggested that the nanorods adsorbent could adsorb silver ions in AMD well. Based on the adsorption/desorption study result, the adsorbent can be efficiently recovered.

Key words | adsorptive, Ag$^{+}$, ionic liquids, polyoxometalates, response surface methodology (RSM)

INTRODUCTION
Ionic liquids (ILs) have been widely used and found extremely high interests in almost all application fields of chemistry, especially in separation science. Many researchers have investigated ILs for the extraction and separation of metal cations. Papaiconomou et al. described that extractions were performed with four new task-specific ionic liquids. Such liquids containing a disulfide functional group are efficient and selective for mercury and copper, whereas those containing a nitrile functional group are efficient and selective for palladium (Papaiconomou et al. 2007). More studies have suggested that Au, Pd, Pt and Ag nanoparticles could immobilize in ILs (Ki-Sub et al. 2005). Besides, ILs with unique and fascinating properties can act as both templates and precursors to functional materials. Snyder et al. attempted to encapsulate a hydrophobic, protic IL into the pores of Ni-Pt alloy nanoparticles (Snyder et al. 2010). The study found that this practice could produce a high surface area and sometimes nanoporous catalysts with a Pt-enriched outer surface.

Polyoxometalates (POMs) are an eternal hot topic. On the one hand, the thought of molecular design has become an important research strategy. On the other hand, the porous materials based on POMs have the advantages of excellent adsorption properties and environmental performance. Currently, the researchers have used zeolite, SiO$_2$, activated carbon as carrier which is loaded on with POMs to increase the specific area of POMs. Although that could enhance the mechanical properties and thermostabilities of POMs, the problems such as the physical structure is disordered, which limits the application of POMs. Because the POMs molecule is bulky, polyhedral and rigid, it is difficult to control the physical structure, although a few studies reported some ordered arrangement of nanostructure...
Composites based on POMs. Park (Park et al. 2013) successfully synthesized a well-oriented dandelion-shaped porous silica spheres (DSS) that supported heteropolyacids (HPA) catalyst for the dehydration of n-butanol. The HPA/DSS showed a higher conversion and yield than HPA supported on SBA-15 or microporous silica in liquid-phase dehydration of n-butanol to di-n-butyl ether. Ćirić-Marjanović et al. (2010) has doped 12-tungstophosphate (WPA) to polyaniline (PANI). Due to the addition amounts of WPA, the morphological of PANI-WPA showed nanotubes or nanorods. And the new micro/nanostructured PANI-WPA materials could be applied as catalysts and sensors. Thus, it can be seen that the properties of regular heteropolyacid compounds are superior to amorphous. It is pointed out that scholars have done many studies on the IL-POM based molecular salt focuses on catalysis. Some studies showed that the molecular salt could adsorb metal ions to act as catalysis. This indicates the IL-POM based molecular salt could be used as adsorbent (El-Naggar et al. 2013). Classical approaches for the optimization require a very large number of experiments to be performed, which would be very expensive and time consuming. For optimization of adsorption process parameters, response surface methodology (RSM) was opted. The RSM is a collection of mathematical and statistical techniques which is useful for optimizing process parameters. The liquid–solid interface adsorption process is mainly influenced by various parameters such as pH, initial concentration, temperature, adsorbent dose, contact time and others. In this work, a central composite design (CCD) approach was applied to decide the number of the adsorption experiments to be performed for optimization of the process variables.

Excessive exploitation and improper disposal are attributed to be prime factors responsible for the release of heavy metals into the environment. The acid mine drainage (AMD) that generated from zinc slag of the hydrometallurgy process, contains high concentrations of Zn$^{2+}$ and Pb$^{2+}$ still with lower concentrations of Ag$^{+}$ and others (Liu et al. 2012). On the one hand, silver ions could be accumulated in organisms (including humans) through the food chain, and then would do harm to their body. On the other hand, silver is a kind of noble metal and a very useful raw material in various industries. So it is necessary to bring silver to permissible limits and to recover it. The conventional method to remove metals is the ion-exchange, but it is infeasible for the AMD that generated from zinc slag of hydrometallurgy process. Because the high concentrations of Zn$^{2+}$ and Pb$^{2+}$ would be participated in the process of ion exchanging to compete with silver ion. For other methods like precipitation, liquid–liquid extraction (Tian et al. 2016) and adsorption, most of them are effective in alkaline or weak acid solutions due to the competitive blinding of protons under acidic conditions (Pourreza et al. 2014). Nevertheless, the spot pH of AMD is almost 2–5. So, the pH of the Ag$^{+}$ solutions has been set to ensure high adsorption properties of the adsorbents.

Herein, a water-tolerant material based on ILs, namely [n-3BBIM]$_9$PW$_9$O$_{34}$, was synthesized by the simple molecular assembly. The electron mobility of IL-cations and HPA-ions composite will be enhanced compared with HPA. And the adsorbent showed high selectivity adsorption abilities to silver ions with high concentrations of Zn$^{2+}$ and Pb$^{2+}$ at low pH levels. The influence of pH, initial metal concentration and adsorbent dosage on the elimination of silver ions from aqueous solution were also studied by RSM.

**EXPERIMENT**

**Preparation of [n-3BBIM]$_9$PW$_9$O$_{34}$**

The reagents were of analytical grade and ultra-pure water was used in the preparation and dilution of various aqueous solutions. The Keggin lacunary heteropolytungstate PW$_9$ was synthesized according to the literature procedure (Okun et al. 2005). 1-n-Butyl-3-butylimidazolium bromide ([n-3BBIM]Br) was prepared following the procedure (Li et al. 2013). $^1$H NMR (400 MHz, CDCl$_3$, δ/ppm):10.46 (s, 1H), 7.55(s,1H), 7.32(s, 1H), 4.38(t, 2H), 4.36(t, 2H), 1.94 (m, 2H), 1.90(m, 2H), 1.40(m, 2H), 1.36(m, 2H).

[n-3BBIM]$_9$PW$_9$O$_{34}$ was synthesized according to the procedure in the literature (Huang et al. 2014). 1-n-butyl-3-butylimidazolium bromide (50 mmol) was added dropwise to a solution of PW9 (4 mmol) in 30 mL deionized water and the mixture was stirred at room temperature. The white precipitate immediately formed and the suspension continued being stirred for 2 h. Then the suspension was transferred into a centrifuge at 2,000 rpm for 12 h. The resulting precipitate was washed with distilled water, filtered and dried at 80 °C overnight. The yield was about 86%.

**Characterization of the adsorbent**

Infrared adsorption spectra were obtained by Fourier transform infrared (FT-IR) spectrometer (TENSOR 27, Bruker, Germany) using KBr disc. The interaction between silver ion and heteropolytungstate were characterized by ultraviolet-visible (UV-Vis) absorption spectrometer (TU-1810, Beijing’s General Instrument Co., Ltd, China). Surface
morphology was observed by scanning electron microscope (SEM) (S-480, Hitachi, Japan). The crystal structures of the samples were characterized by X-ray diffractometer (XRD) (D8 FOCUS, Bruker, Germany). The concentrations of the metal ion residual were determined by atomic absorption spectrometer (AAS) (SOLAAR M6, Thermo, USA).

Batch adsorption experiments with CCD

The methodology of experimental design was used for modeling and optimization of the adsorption processes of Ag\(^{+}\) from aqueous solutions. In this experiment, we have set the pH, initial concentration, adsorption dosage and temperature as single-factor (Lakhdhar et al. 2013). On the basis of the univariate of optimal value, three parameters, initial concentration (X₁), adsorbent dosage (X₂) and temperature (X₃), were studied by using Design-Expert 8.0.5b. The mathematical relationship between the three variables can be approximated by the second-order polynomial model (Ahmady-Asbchin et al. 2013):

\[
Y = \beta_0 + \sum_{i=1}^{n} \beta_iX_i + \sum_{i=1}^{n} \beta_{ii}X_i^2 + \sum_{i=1}^{n} \sum_{j=1}^{n} \beta_{ij}X_iX_j + e \tag{1}
\]

where \(Y\) is the predicted response, \(\beta_0\) the constant coefficient, \(\beta_i\) the linear coefficients, \(\beta_{ii}\) the quadratic coefficients, \(\beta_{ij}\) the interaction coefficients, \(X_i\) and \(X_j\) are the coded values of the independent process variables, and \(e\) is the residual error.

The design variables selected in this study with coded levels along with response variables are shown in Tables 1 and 2. The modeling is performed by an analysis of variance (ANOVA) of the model and the validated model can be plotted in a tri-dimensional graph, generating a surface response that corresponds to a response function used to determine the optimization of a process.

All batch adsorption experiments were performed on a thermostated shaker with a shaking frequency of 120 rpm. CCD experiments were determined by a single-factor experiment and the studies were conducted to investigate Ag\(^{+}\) adsorption as a function of adsorbent dose (1–4 g/L), pH = 2 (the pH value of AMD is about 2), temperature (20–45 C) and initial concentration of Ag\(^{+}\) (10–300 mg·L\(^{-1}\)). After adsorption equilibrium, the solid materials are separated by filtration with Whatman–42 filter paper (pore size 2.5 μm). The total Ag\(^{+}\) concentration is measured by an atomic absorption spectrometer (AAS). The adsorption percentage is calculated as the following Equation (1):

\[
\text{Removal} = \left[ \frac{C_0 - C_e}{C_0} \right] \times 100\% \tag{2}
\]
where $C_0$ and $C_e$ were the initial and equilibrium concentrations of solutions (mg/L), respectively. Removal percentage values were recorded as the response of the system and the values were used in creating the surface plots.

**Selectivity experiments**

In order to prove Ag$^{+}$ specificity of the adsorbent, Zn(II) or Pb(II) was chosen as a competitive ion, respectively. The concentration of Ag$^{+}$ was kept at 150 mg/L, the one for the competitive ion was kept at 10–300 mg/L and pH was kept at 2.0. The experiments were carried out by batch adsorption. The concentrations of the ions’ residual in the solution were determined by AAS. The selectivity parameters were calculated as the following Equations (3) and (4):

$$K_d(X) = \frac{C_0,X - C_i,X}{C_i,X} \times \frac{V}{m}$$  

where $K_d$ represents the distribution coefficient, $C_0,X$ represents the initial concentration of X, $C_i,X$ represents the ion residual of X, $\alpha$ represents the relative selectivity coefficient, and X(II) represents Zn(II) or Pb(II).

**Adsorption–desorption experiments**

The experiments were studied in a batch system. Firstly, 0.5 g of [n-BBIM]$\_9$PW$_{9}$O$_{34}$ was added in 50 mL of 1,000 mg/L Ag$^{+}$ solution without adjusting the pH and then the suspensions were shaken for 12 h (250 rpm) at room temperature, filtered through a filter paper and rinsed with deionized water. Then, desorption experiments were carried out using 1 mol/L HNO$_3$ and shaken with a constant stirring (250 rpm) at room temperature, filtered through a filter paper, rinsed, dried at 353 K. The desorption efficiency was calculated using the following equation:

$$D_E = \frac{C_d \times V_d}{(C_0-C_e) \times V_0} \times 100\%$$

where $D_E$ is desorption efficiency (%), $C_d$ is equilibrium concentration of Ag$^{+}$ desorbed (mg/L), $V_d$ is the volume of desorbed solution, $C_0$ represents the initial concentration of Ag$^{+}$, $C_e$ represents the ion residual of Ag$^{+}$ and $V_0$ is the volume of sorbed solution.

**RESULTS AND DISCUSSION**

**FT-IR spectrum characterization**

The corresponding peak changes (Figure 1) in the spectrum of [n-BBIM]Br, [n-BBIM]$\_9$PW$_{9}$O$_{34}$ and after adsorption of silver ion were confirmed by the FT-IR spectral analysis. The spectra clearly show different regions of stretches characteristic of [PW$_{9}$O$_{34}$]$^{9-}$ (500–1,100 cm$^{-1}$) and n-BBIM cation (1,100–1,600 cm$^{-1}$ and 2,700–3,200 cm$^{-1}$). The four characteristic bands for the Keggin structure of [PW$_{9}$O$_{34}$]$^{9-}$ appeared at 1,056 cm$^{-1}$, 1,010 cm$^{-1}$, 886 cm$^{-1}$ and 817 cm$^{-1}$ (see attached chart), assignable to vibrations of $\pi$ electrons from organic cations to inorganic anions (Elaivi et al. 1995). Consequently, the electron density of [PW$_{9}$O$_{34}$]$^{9-}$ anions increased, which leads directly to attach cations (like Ag$^{+}$) easily. Furthermore, the bands at 1,162 cm$^{-1}$ and 2,870 cm$^{-1}$ for [n-BBIM]Br belongs to the imidazole C-N stretching and methylene C-H stretching vibrations, and have shifted to 1,162 cm$^{-1}$ and 2,868 cm$^{-1}$ for [n-BBIM]$_9$PW$_{9}$O$_{34}$, respectively. This
result indicates the ionic linkage and hydrogen bonding interactions between the IL-cations and HPA-anions (Zhao et al. 2013). After silver adsorption, changes were observed in IR spectra with the P–O_a, W–O_{b\text{(c)}}–W and M–O_d peaks hypsochromic shifting. Minimal movement demonstrates Ag^+ has complexed with [n-BBIM]_9PW_9O_34, but the basic structure and geometry of the Keggin anion were preserved, verifying a rather durable adsorption structure.

**UV-Vis spectral characterization**

In order to explicitly show the adsorption mechanism, the charge transfer behavior of Keggin anion and Ag^+ is shown in Figure 2.

The UV-Vis spectra of PW_9 are shown in the inserted chart in Figure 2. The electronic band at \( \lambda_{\text{max}} = 247 \text{ nm} \) is characteristic of Keggin structure and is attributed to the ligand-to-metal-charge transfer transition (LMCT) from the bridging oxygen atoms O_b and O_c to W (O_{b\text{(c)}} \to W). The band at \( \lambda_{\text{min}} = 206 \text{ nm} \) is attributed to the LMCT transition from the terminal oxygen atoms to the W (O_d \to W) (Min et al. 2005). With the increasing of Ag^+ concentration, the characteristic absorption bands are obviously red-shifted compared to PW_9. It is well-known that the Ag(I) has better electron affinity properties than W(V) or W(VI). When the silver ions complexed with [n-BBIM]_9PW_9O_34, making electrons O_{b\text{(c)}} and O_d pass from W to Ag, which led to the bound energy required between O_{b\text{c/d}} and W being reduced, and the wavelength of O_{b\text{(c)}} \to W and O_d \to W was red-shifted accordingly. From an energetic standpoint, the type of electron transition belongs to charge-transfer for the heteropolyacid. Further, the nature of charge-transfer is a redox process (Ma & Liu 2007). This also goes to show that electrons transfers from [PW_9O_34]^9- to Ag^+ (Bonfim et al. 2014).

**SEM and energy dispersive X-ray studies**

The images from scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were used to compare the surface morphological features of the adsorbent before and after Ag(I) adsorption (Figure 3). From Figure 3(a), it could be seen that the adsorbent surfaces were smoother without any granules and the structure looks like regular barred. But after adsorption, the surface of the adsorbent turned to be rough, crude and anomalous. This illustrated that other substances could be well adsorbed by the adsorbent. To verify whether the electron dense part on the surface of the adsorbent is made up of silver ions, EDX analysis was applied. While the EDX (a) did not show the characteristic peak of silver, (b) for the adsorbent after adsorption there appeared the peak of silver. It is illustrated that the silver has adhere to the adsorbents.

**X-ray diffraction analysis**

X-ray diffraction patterns of the adsorbent before and after adsorption of silver are given in Figure 4(a) and 4(b). Before adsorption, the [n-BBIm]_9PW_9O_34 presented a set of diffraction peaks for the secondary structure of the inorganic heteropolyacid crystal (Zhao et al. 2013). After adsorption, some characteristic peaks of PW_9 disappear, which implies that during the adsorption, the structure of PW_9 is rearranged by adsorption of silver ions, but its skeleton is reserved after adsorption. And some new peaks emerged at \( 2\theta = 38.1 ^\circ \) (111), \( 44.5 ^\circ \) (200), \( 64.4 ^\circ \) (220), and \( 77.4 ^\circ \) (311), suggesting successful reduction of silver metal at the adsorbent surface (Amin et al. 2009) and the Ag nanometer crystals are cubic crystals. It is consistent with the result from the EDX.

**Effect of pH on silver ions adsorption**

In most cases, the solution pH is one of the parameters that has strong influence on metal adsorption due to the protonation or deprotonation of ligand active sites that would affect the binding ability with metal species. In strong acid solution, the surface hydroxyl groups would not dissociate and, therefore, the adsorption of Ag^+ species could rarely occur. Moreover, the spot pH of AMD is almost 2–5. So in this study, the solution pH was varied in the range of 1 to 7, and adsorbent dose (2.5 g/L), temperature (25 C) and
initial concentration of Ag\(^+\) (150 mg/L). After adsorption equilibrium, the adsorption efficiency of [n-BBIM]\(_9\)PW\(_9\)O\(_{34}\) is shown in Figure 5. The results show that the removal of Ag\(^+\) is almost closely to 94% in the pH range of 1–5 according with the AMD. So the pH of AMD has no effect on the efficiency of the adsorbent. It is maybe that the adsorbent is stable in acid solution.

**Figure 3** | The SEM and EDX of adsorbent: (a) before adsorption, (b) after adsorption of silver ions.

**Figure 4** | X-ray diffraction pattern of adsorbent: (a) before adsorption, (b) after adsorption.

**CCD**

As the pH of AMD has no effect on the adsorbing effect from AMD, three independent variables (Ag\(^+\) concentration \(X_1\), adsorbent dosage \(X_2\) and temperature \(X_3\)) were prescribed into three levels (low, basal and high) with coded values \((-1, 0, 1)\) and the star points of \(+\alpha\)
and $\alpha$, respectively, were selected for each set of experiments are presented in Table 1. Twenty experiments for the optimization were performed according to the CCD and their responses are presented in Table 2. The main interaction and quadratic effects were evaluated in this design. To find the most important effects and interactions, the analysis of variance (ANOVA) was calculated using Design-Expert 8.05 (Table 3). Data analysis gave a second order polynomial model of removal (%) with the following Equation (6):

$$
\text{Removal} = 6.10320 + 0.32545X_1 + 39.43646X_2 + 1.42156X_3 + 0.35550X_1X_2 - 1.33333 \times 10^{-3}X_1X_3 + 6.50000 \times 10^{-3}X_2X_3 - 4.70411 \times 10^{-3}X_2^2 - 15.87414X_2^3 - 0.021477X_3^3
$$

Results observed in Table 2 suggest the suitability of regression model for Ag$^{+}$ adsorption on nanoparticles. The predicted values are quite close to the experimental results. ANOVA test for model is presented in Table 3. A p-value less than 0.05 in the ANOVA table indicates the statistical significance of an effect at 95% confidence level. F-test was used to estimate the statistical significance of all terms in the polynomial equation within 95% confidence interval. The ‘F-value’ of 3.33 implies that the ‘Lack of fit’ is not statistically significant compared with the value of pure error. The linear terms of $X_1$, $X_2$, $X_3$, the quadratic terms of $X_1^2$, $X_2^2$, $X_3^2$ and the interaction $X_1 \times X_2$ are significant in this case. The correlation coefficient of 0.9924 and low values that relate to the model errors indicate that the proposed model was successfully served in the Ag$^{+}$ adsorption from water.

Figure 6 shows that the predicted values of the model response correlated with the observed (actual) values. The

![Figure 5](https://iwaponline.com/wst/article-pdf/74/4/1005/459418/wst074041005.pdf)

**Figure 5** | Effect of pH on the removal of silver ions (initial concentration $= 150$ mg L$^{-1}$, adsorbent dose $= 2.5$ g L$^{-1}$, and the temperature is 25°C).

### Table 3 | ANOVA test for CCD in the case of Ag$^{+}$ adsorption

<table>
<thead>
<tr>
<th>Source</th>
<th>Sum of squares</th>
<th>Df</th>
<th>Mean square</th>
<th>F value</th>
<th>Prob &gt; F</th>
<th>Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
<td>2,170.33</td>
<td>9</td>
<td>241.15</td>
<td>144.41</td>
<td>&lt;0.0001</td>
<td>significant</td>
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<tr>
<td>$X_1$</td>
<td>729.96</td>
<td>1</td>
<td>729.96</td>
<td>437.12</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>$X_2$</td>
<td>633.19</td>
<td>1</td>
<td>633.19</td>
<td>379.17</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>$X_3$</td>
<td>105.48</td>
<td>1</td>
<td>105.48</td>
<td>63.17</td>
<td>0.0008</td>
<td></td>
</tr>
<tr>
<td>$X_1X_2$</td>
<td>227.48</td>
<td>1</td>
<td>227.48</td>
<td>136.22</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>$X_1X_3$</td>
<td>1.28</td>
<td>1</td>
<td>1.28</td>
<td>0.77</td>
<td>0.4018</td>
<td></td>
</tr>
<tr>
<td>$X_2X_3$</td>
<td>$8.450 \times 10^{-3}$</td>
<td>1</td>
<td>$8.450 \times 10^{-3}$</td>
<td>$5.060 \times 10^{-3}$</td>
<td>0.9447</td>
<td></td>
</tr>
<tr>
<td>$X_1^2$</td>
<td>262.88</td>
<td>1</td>
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<td>157.42</td>
<td>&lt;0.0001</td>
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<tr>
<td>$X_2^2$</td>
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<td>1</td>
<td>231.25</td>
<td>138.48</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>$X_3^2$</td>
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<td>58.12</td>
<td>34.81</td>
<td>0.0002</td>
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<tr>
<td>Residual</td>
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<td>10</td>
<td>1.67</td>
<td></td>
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<tr>
<td>Lack of fit</td>
<td>12.84</td>
<td>5</td>
<td>2.57</td>
<td>3.33</td>
<td>0.1066</td>
<td>not significant</td>
</tr>
<tr>
<td>Pure error</td>
<td>3.86</td>
<td>5</td>
<td>0.77</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cor total</td>
<td>2,187.03</td>
<td>19</td>
<td></td>
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</tr>
</tbody>
</table>

$r^2 = 0.9924$. 

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data points are distributed relatively close and have linear behavior. As a result, these plots indicate adequate agreement between real and obtained data.

The relation between various adsorption parameters and the response can be explained by the examination of response 3D surface figure and contour plots as a function of two factors by holding the rest factors at a central level. The effect of Ag\(^{+}\) concentration and adsorbent dosage on the adsorption of Ag\(^{+}\) are presented in Figure 7(a) and 7(b). In the case of adsorption, the initial concentration of Ag\(^{+}\) has a greater influence on the removal rate of Ag\(^{+}\) compared to the adsorbent dosage. The removal rate of Ag\(^{+}\) gradually decreased as the initial concentration of Ag\(^{+}\) increased. One cause may be that the adsorbent has reached its saturated adsorption capacity. The quadratic model equations have been optimized using quadratic programming to maximize adsorption of Ag\(^{+}\) within the experimental range studied. The optimal adsorption conditions for adsorption of Ag\(^{+}\) have been determined as initial concentration 143.33 mg/L, adsorbent dosage 2.69 g, temperature 35.15 °C to achieve the maximum adsorption of Ag\(^{+}\) 99.03% and consistent with the predicted result 100%.

### Adsorption selectivity

In order to investigate the selective properties of the adsorbent, Zn(II) and Pb(II) were chosen as competitive ions individually because of their exit widely in AMD and affect on silver recycling. The distribution coefficient ($K_d$) and the selectivity coefficient ($\alpha$) were shown in Table 4. The results suggested that the adsorbent has a higher distribution coefficient and selectivity. This indicates that the adsorbent can be chosen for the removal Ag treatment in AMD.

### Desorption behavior

The reusability of the adsorbent was investigated in five adsorption–desorption cycles and the adsorption capacities are shown in Figures 8 and 9. As shown in Figure 8, the desorption capacity of Ag\(^{+}\) increased with time growing. The desorption capacity reached its maximum after 6 h and the process was in the state of adsorption–desorption dynamic equilibrium after 15 h. As shown in Figure 9, the adsorption capacity of Ag\(^{+}\) decreases slightly after three consecutive adsorption–desorption cycles. After being recycled five times, the
adsorption capacity changes from 74.3 mg/g to 38.8 mg/g. What calls for special attention is that the quality of the [n-BBIm]9PW9O34 has reduced from 0.50 g to 0.39 g after using three times, which caused the adsorption capacity of Ag⁺ on adsorbent declined. On the other hand, the desorption efficiency did not change evidently as the number of adsorption–desorption cycles increased. So, the Ag⁺ can be recovered efficiently and the adsorbent can be reused though with the decreasing of adsorption capacity.

**Various adsorbent for Ag(I) removal**

A comparison of removal using different adsorbents has been made and presented in Table 5. As it can be seen, the proposed adsorbent is superior or comparable to other adsorbent in terms of high adsorption capacity. This adsorbent is suitable for the high removal of Ag(I) even in strong acidic solution, while other adsorbents cannot compete with this for adsorption in acid solution with high efficiency. This fundamental study will be helpful for further application in designing a batch adsorption system for the treatment of silver ions containing effluent coming out from AMD.

**CONCLUSION**

In this study, we have used the ILs as precursors to functional POMs to synthesize an adsorbent with uniform, clavate nanostructures by a simple molecular assembly. The adsorbent has a high adsorption efficiency of Ag⁺ in AMD without any pH-adjusting. The adsorbent is characterized by IR, SEM and XRD and so on. IR showed the redox properties of the adsorbent being improved by the strong electronic interaction between the π–electron enriched imidazole framework and...
HPA anions. The adsorption was determined and optimized using single-factor experiments and RSM. CCD has been used to model and optimize the influence of process parameters on adsorption of Ag⁺. The optimal adsorption conditions such as initial concentration of Ag⁺, adsorbent dosage and the adsorption temperature have been worked out, with a maximum adsorption of Ag⁺ 99.03%, which is consistent with the predicted result of 100%. The selective experiments show that the adsorbent can be chosen for removal Ag⁺ treatment in AMD and are expected to be useful in many other water pollution under high background of Zn²⁺ or Pb²⁺. Desorption studies showed that [n-BBIm]₉[PW₆O₃₄] could be regenerated using diluted nitric acid, and high desorption efficiency was held in five adsorption–desorption recycles.

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REFERENCES


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