Green Synthesis of Reusable Adsorbents for the Removal of Heavy Metal Ions
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ABSTRACT: Industrial wastewater often contains heavy metals, like lead, copper, nickel, cadmium, zinc, mercury, arsenic, and chromium. Overdoses of heavy metals will impose a severe threat to human health. Adsorption is the most efficient way of wastewater treatment for eliminating heavy metals. A novel material-reusable hydrogel-based adsorbent was developed in overcoming the regeneration issue. The polyethylene glycol diacrylate-3-sulfopropyl methacrylate potassium salt (PEGDA-SMP) hydrogel performed an ion-exchange rate to remove heavy metals from wastewater in 30−120 min. The adsorption capacity of PEGDA-SMP increases the increasing pH of a solution, in which pH 5 reaches the maximum. Pseudo-second-order adsorption and the Langmuir adsorption model can fully describe the adsorption properties of PEGDA-SMP for heavy metals. PEGDA-SMP prefers to exchange Pb^{2+} through K^+, and its adsorption capacity can achieve 263.158 mg/g. Ag^+, Zn^{2+}, Ni^{2+}, and Cu^{2+} were 227.27, 117.647, 102.041, and 99.010 mg/g, respectively. The hydrated ionic radius of the heavy metal might play an essential role to affect the adsorption preference. The removal efficiency of heavy metals can approach over 95% for each heavy metal. PEGDA-SMP performs rapid desorption and reaches desorption equilibrium in 15 min. After 10 consecutive adsorption−desorption cycles, the adsorption capacity remained over 90%. The hydrogel developed in this study showed reversible heavy metal absorption. Therefore, excellent adsorption−desorption properties of PEGDA-SMP can be potentially extended to industrial wastewater for removing heavy metals.

1. INTRODUCTION
Heavy metals are referred to as a group of metals and metalloids with an atomic weight between 63.5 and 200.6 g mol⁻¹ and densities greater than 5 g cm⁻³.¹⁻³ Common examples of heavy metals are Pb, As, Hg, Cd, Zn, Ag, Cu, Fe, Cr, Ni, Pd, and Pt.¹⁻³ Water pollution is caused due to discharge of heavy metals from anthropogenic sources such as mining, mineral processing, metallurgical operations, electroplating, fuels, painting, battery manufactures, paper, pigments, photographic materials, and explosive manufacturing.¹⁻³ Most heavy metals are non-biodegradable and can be bioaccumulated through food chains into higher trophic levels, resulting in deteriorating effects on living species.⁴⁻⁶ If they are adsorbed above the permissible levels to the human body, they can lead to serious health effects such as immune system and reproductive system diseases, accumulative poisoning, and cancers.⁴⁻⁶ Consequently, environmentalists have been concerned about the research to develop effective technologies to remove and reuse these heavy metals from wastewater before being discharged into the environment.⁴⁻⁶ The conventional methods for the removal of heavy metals from wastewater are ion exchange,⁹⁻¹⁰ solvent extraction,¹¹ electrolysis,¹² precipitation,¹³ ion floatation,¹⁴ reverse osmosis,¹⁷ and adsorption.¹⁷ Most of these methods are associated with the generation of toxic sludge which has secondary environmental pollution due to its non-eco-friendly nature. Hence, in the recent past, adsorption has emerged out as an effective, environmentally friendly, and economical alternative approach for wastewater treatment.⁴ The adsorption capability of an adsorbent depends on the surface active sites which occur due to the presence of functional groups on the adsorbent (such as carboxyl, hydroxyl, amino, and hydrosulfonyl).¹⁵ The metal ions are attached to the surface of the adsorbent through physical or chemical interactions, and then, these ions are adsorbed mainly by ion exchange, electrostatic interactions, coordination interactions, physical adsorption, or chemical interactions. The heavy metals are present in wastewater at low concentrations, and the
adsorption method is appropriate even when the concentrations of metal ions are as low as 1 mg/L. Other advantages of this method are low initial and operation cost, unproblematic design, easy operation, and high efficiency. Numerous adsorbents have been developed and experimented with to remove metal ions from wastewater, including biomass adsorbents, activated carbon, inorganic minerals, chelating resins, ion-exchange resins, and so forth. Among them, nowadays, ion-exchange resins are focused due to their efficient adsorption capacity and high selectivity toward specific metal ions. An ion-exchange resin consists of two components: the first one is a functional group that forms the electrostatic interaction with metal ions and the second is the support, which is a polymeric matrix. The functional groups in the adsorbent contain one or two donor atoms that are protonated in a low-pH medium, resulting in the complex formation with metal ions.

Hydrogels are different functional group-containing materials that can be chemically modified to a specific task such as metal ion adsorption. Poly(ethylene glycol) diacrylate (PEGDA) having a three-dimensional network structure is an extremely hydrophilic and colorless hydrogel that is used in chemicals, cosmetic products, and medicine, including stem cell transplantation, contact lenses, and so forth. This polymer forms through certain chemical and physical cross-linking. The density of PEGDA is less than that of traditional resins, and as the water content increases, the volume of the hydrogel is expanded and the pore size is increased. This has characteristics of high hydrophilicity, photodegradability, non-toxicity, and biocompatibility. This PEGDA hydrogel surface can be used as an anchor site for introducing functional groups such as sulfonic groups (−SO3H), amino groups (−NH2), carboxylic groups (−COOH), and hydroxyl groups (−OH). The adsorption mechanism between the functional groups of −COOH, −SO3H, and phosphonic (−PO(OH)2) groups and metal ions has been ascribed to ion exchange and electrostatic interactions.

This work is aimed at the green synthesis of reusable hydrogel-based adsorbents, polyethylene glycol diacrylate-3-sulfopropyl methacrylate potassium salt (PEGDA-SMP). The modified hydrogel surface can be used as an anchor site for introducing functional groups such as sulfonic groups (−SO3H), amino groups (−NH2), carboxylic groups (−COOH), and hydroxyl groups (−OH). The adsorption model, kinetics, and thermodynamics were discussed. Moreover, the adsorption behavior, like the adsorption model, kinetics, and thermodynamics were also investigated.

2. RESULTS AND DISCUSSION

2.1. Characterization of the Hydrogel Adsorbent. The Fourier transform infrared (FT-IR) spectrum as shown in Figure 1 illustrates the distinct bands which indicate the presence of functional groups in SMP, PEGDA, and the PEGDA-SMP-modified hydrogel. Figure 1a represents the FT-IR spectrum of SMP. The adsorption band at 2920 cm−1 is assigned to the CH stretching vibration, and adsorption bands at 1726, 1646, and 1454 cm−1 are assigned to CH bending vibrations of SMP. The band at 1043 cm−1 indicates the S=O stretching vibration. Figure 1b illustrates the FT-IR spectrum of the PEGDA hydrogel only. The broad band at 3500 cm−1 occurs according to −OH in moisture, which is caused by the high hydrophilicity of the hydrogel. Adsorption bands at 2880 and 1450 cm−1 confirm the tensile vibration and bending vibration of −CH, respectively, while 1740 cm−1 is due to the main characteristic functional group of the PEGDA hydrogel, and this indicates the tensile vibration of ester O=CO. Bands around 1680 and 953 cm−1 reveal C=C bending vibrations, while the bands at 1290 and 1100 cm−1 are attributed to the bending vibration of alcohol −OH and the tensile vibration of COC, respectively. Figure 1c shows the FT-IR spectrum of the PEGDA-SMP-modified hydrogel. According to this, it can be observed that the stretching vibration of −CH of PEGDA has shifted from 2880 to 2950 cm−1, and the stretching vibration of O=CO and COC of esters has shifted to 1716 and 1196 cm−1, respectively, which are characteristic features of PEGDA. The characteristic peak of SMP is shifted to 1058 from 1043 cm−1, which is due to the stretching vibration of S=O. According to the above illustration, the characteristic peaks of PEGDA and SMP can be found on the FT-IR spectrum of the PEGDA-SMP-modified hydrogel, confirming that the PEGDA-SMP hydrogel is successfully modified.

Figure 2a–c presents the scanning electron microscopy (SEM) image of PEGDA-SMP within different magnifications, and its surface performs smoothly without any porous structure. To confirm the adsorption ability of PEGDA-SMP toward five metal ions [Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II)], the spent PEGDA-SMP hydrogels were analyzed by SEM/EDS shown in Figure 2d–h. All metal ions were observed either on the surface or inside of PEGDA-SMP hydrogels, indicating the adsorption ability of PEGDA-SMP hydrogels.

2.2. Effect of Initial Concentration of the Adsorbate. Adsorption experiments at initial heavy metal concentrations from 100 to 300 mg/L were also performed with fixed other parameters. The results (Figure 3a) indicate that Qe were not intensely increased with the increasing initial concentrations of Ni, Cu, and Zn. However, for Ag, Qe increased with Co.
compared to other heavy metals. When considering the behavior of selected heavy metals, 100 mg/L was selected for further experiments as it showed more than 90% of heavy metal removal.

Figure 2. SEM image of the synthesized PEGDA-SMP hydrogel: (a) 100× magnification, (b) 250× magnification, and (c) 1000× magnification; EDS for the spent PEGDA-SMP hydrogel: (d) Ag(I), (e) Ni(II), (f) Zn(II), (g) Cu(II), and (h) Pb(II).

Figure 3. Effect of different parameters on the adsorption of Ag(I), Cu(II), Ni(II), Pb(II), and Zn (II). (a) Effect of initial concentration of the adsorbate ($W = 250$ mg, $V = 500$ mL, $pH = 5$); (b) effect of different pH ($C_0 = 100$ mg/L, $W = 5$ mg, $V = 10$ mL, 25 °C); (c) effect of contact time ($C_0 = 100$ mg/L, $W = 250$ mg, $V = 500$ mL, $pH = 5$).
2.3. Effect of pH on Heavy Metal Ion Adsorption. The pH of the solution directly influences the adsorption efficiency of metal ions since it influences the surface charge of the adsorbent.\textsuperscript{7,28} From the experimental results shown in Figure 3b, metal ion adsorption of the PEGDA-SMP adsorbent was increased with the increasing pH and had maximum adsorption at pH 5. It can be observed that PEGDA-SMP has the best adsorption effect on Pb(II), and then Ag(I), followed by Zn(II), Ni(II), and Cu(II). SMP is a strong acid cation exchanger with the negatively charged functional group of sulfonate (SO\textsubscript{3}H) which can easily dissociate and adsorb other cations in the medium. This concept is called ion exchange,\textsuperscript{7} and the reaction mechanism can be illustrated as eqs 1 and 2. H\textsuperscript{+} concentration in a solution is inversely proportional to the pH of the solution. At a lower pH value, the adsorption capacity of metal ions is decreased due to the presence of high H\textsuperscript{+} in the medium which competes with metal ions for the sorption sites on the adsorbent. The negative charge nature of the adsorbent is increased with the increasing pH of the medium, and this leads to an increase in the electrostatic interaction between cationic metal ions and the anionic adsorbent surface.\textsuperscript{30} When the pH increases into a basic value, it tends to form metal hydroxide and precipitate and hence decrease the adsorption capacity with higher pH values.\textsuperscript{7,30}

\[ -\text{SO}_3^-\text{K}^+ + \text{H}^+ \rightarrow -\text{SO}_3^-\text{H}^+ + \text{K}^+ \]  
\[ -\text{SO}_3^-\text{K}^+ + \text{M}^+ \rightarrow -\text{SO}_3^-\text{M}^+ + \text{K}^+ \]

When considering the zeta potential effect, an increment of pH leads to compression of the electrochemical layer of the adsorbent, resulting in a decreased zeta potential. However, the sulfonate group exhibited a strong negative charge at all ranges of pH.\textsuperscript{31} Therefore, a lower adsorption capacity at low pH was mainly contributed by competition between protons and metal ions.

2.4. Adsorption Kinetics and Thermodynamics. The effect of contact time on metal adsorption is shown in Figure 3c. The experimental results show that PEGDA-SMP has a very fast adsorption rate toward heavy metal ions in the medium. It only took 30 min for Cu(II), Ni(II), and Zn(II) but 90 and 120 min for Ag(II) and Pb(II), respectively, to reach adsorption equilibrium.

The parameters for pseudo-first-order and pseudo-second-order models that were used to evaluate the kinetic mechanism which controls the adsorption process are shown in Table 1. The elucidation of the pseudo-first-order model is a second-order reaction, and the elucidation of the pseudo-second-order kinetic model is a tertiary reaction.

According to the interpreting data, adsorption of Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II) on PEGDA-SMP adsorbents was fitted with the pseudo-second-order kinetic model. The correlation coefficient ($R^2$) of the pseudo-second-order kinetic model for adsorption was above 0.99 for all heavy metals, and in the pseudo-first-order kinetic model, only those for Ag(I) and Zn(II) were above 0.99. In addition, the equilibrium adsorption capacities of Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II) ions calculated from the pseudo-second-order ($Q_e$) were 126.58, 85.47, 86.20, 208.33, and 161.29 mg/g, respectively, which were consistent with the experimental values of 111.01, 92.47, 94.65, 192.11, and 87.81 mg/g, respectively. However, $Q_e$ values calculated from the pseudo-first order for heavy metals had a significant difference with the experimental data. Analysis diagrams for pseudo-first-order and pseudo-second-order models are shown in Figure 4.

The activation energies for heavy metal adsorption onto the PEGDA-SMP hydrogel obtained from the slope of the plot of ln $k_2$ versus 1/$T$ (Figure 5a) were found to be 15.69, 1.31, 8.43, 32.27, and 12.41 kJ mol\(^{-1}\) for Ag(I), Ni(II), Zn(II), Cu(II), and Pb(II), respectively. As indicated in Figure 5b, $Q_e$...
is decreased with the increasing temperature, indicating that the bonding between heavy metals and the active sites of the PEGDA-SMP adsorbent weakened at higher temperature and hence, the adsorption process is exothermic.

2.5. Adsorption Isothermal Model. As expressed by the Langmuir model, a monolayer adsorption process occurs on a homogeneous adsorbent surface. Also, the adsorption energy of every active site of the adsorbent is similar. Then, as expressed by the Freundlich model, multilayer adsorption occurs on a heterogeneous adsorbent surface, while the adsorption sites have different affinities toward the adsorbate.\(^\text{32}\) Figure 6 shows the fitted curve for Langmuir and Freundlich models, and their parameters are presented in Table 2. \(R^2\) values and the plotted values indicated that the Langmuir model fits with the experimental data better than the Freundlich model. The calculated \(Q_{\text{max}}\) values of heavy metals, which were obtained from the Langmuir plots, were fitted with the experimentally obtained data, and they were 227.27, 99.01, 102.04, 117.65, and 263.16 mg/g for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II), respectively. This indicates that the adsorption process mainly was monolayer adsorption.

According to the adsorption mechanism, the adsorption of heavy metal ions onto PEDA-SMP happened through the ion-exchange reaction between potassium sulfonate ions in the functional group and metal ions; hence, each potassium sulfonate ion only interacts with a single metal ion and there is no multilayer effect. Also, the Langmuir constants \((K_L)\) for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II) were 0.1146, 0.1774, 0.1774, 0.1778, and 0.0033 L/mg, respectively. The separation factor constants \((R_L)\) of Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II) were 0.0286, 0.0185, 0.0171, 0.3532, and 0.0182, respectively.

2.6. Removal Efficiencies of Single Metal Ions. Experimental results showed (Figure 7) that when the initial concentration of the metal ion was 100 mg/L and the PEGDA-SMP amount was 10 mg, the removal rate of Pb(II) reached more than 90%, while when the PEGDA-SMP amount was 20 mg, the removal rate of divalent metal ions [Cu(II), Ni(II), Zn(II), and Pb(II)] reached more than 99%. However, the removal rate of Ag(I) was about 94.6% when PEGDA-SMP was 50 mg.

The reason for these observations is the hydrated metal ion radius effect. Metal ions in an aqueous medium form hydrates with water molecules, and the hydrated ionic radii of Pb(II), Ag(I), Zn(II), Ni(II), and Cu(II) are 1.19, 1.00, 0.74, 0.69, and 0.60 Å, respectively. As PEGDA is a hydrophilic material, metal ions in the surrounding are easily brought onto the adsorbent in the form of hydrated ions and exchange with K\(^+\) on the adsorbent. When the hydration radius of a metal ion is large, it is easy to react with water molecules since Pb(II) has the highest hydrated ionic radius among the five heavy metal ions and has reached the highest adsorption rate. However, although the hydrated ionic radius of Ag(I) is larger than those of Cu(II), Ni(II), and Zn(II), the removal rate of Ag(I) was
Table 2. Kinetic Parameters for Langmuir Isotherm and Freundlich Isotherm Models (pH 5, C₀ = 100 mg/L, V = 10 mL, 25 °C)

| Metal ions | Q_max (mg/g) | K_L (L/mg) | R_L | R² | N | K_F (L/mg) | R² |
|------------|--------------|-------------|-----|----|---|-------------|----|
| Ag⁺        | 2227.21      | 0.1146      | 0.0286 | 0.9961 | 2.241 | 0.488 | 0.9741 |
| Cu²⁺       | 99.01        | 0.1774      | 0.0185 | 0.9996 | 8.045 | 0.585 | 0.9989 |
| Ni²⁺       | 102.04       | 0.1774      | 0.0171 | 0.9994 | 7.593 | 0.583 | 0.8360 |
| Pb²⁺       | 263.16       | 0.0033      | 0.3532 | 0.9998 | 14.881 | 0.720 | 0.9245 |
| Zn²⁺       | 117.65       | 0.1778      | 0.0182 | 0.9998 | 6.460 | 0.585 | 0.9828 |

Figure 7. Amount of the hydrogel adsorbent on the removal efficiency of Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II). C₀ = 100 mg/L, V = 10 mL, 25 °C, pH = 5).

Figure 8. Amount of the hydrogel adsorbent on the removal efficiency of multiple metal ions present in industrial discharged water (C₀ = 100 mg/L, W = 5 mg, V = 10 mL, 25 °C, pH = 5).

If an adsorbent cannot be desorbed or regenerated effectively, the application value of the adsorbent is reduced and creates secondary environmental pollution. Therefore, HNO₃ was used as the desorptive solvent, and as shown in eqs 3 and 4, a high concentration of H⁺ exchanges with the adsorbed metal ion on the PEGDA-SMP adsorbent.

\[
\text{SO}_3^-\text{K}^+ + \text{M}^+ \rightarrow \text{SO}_3^-\text{M}^+ + \text{K}^+ \quad (3)
\]

\[
\text{SO}_3^-\text{M}^+ + \text{H}^+ \rightarrow \text{SO}_3^-\text{H}^+ + \text{M}^+ \quad (4)
\]

According to the experimental results, when the concentration of HNO₃ was increased, the desorption effect also increased. For example, the desorption rates of Ag(I) were 86.10 and 90.43% when the concentration of HNO₃ was 0.5 and 4 M, respectively. Therefore, 4 M HNO₃ (aq) was selected as the desorption agent to have the best desorption effect.

After desorption, PEGDA-SMP was regenerated using 1 M KNO₃ (aq). The purpose of using KNO₃ was to exchange H⁺ on the functional group of the desorbed sulfonate group with K⁺ and restore PEGDA-SMP into its initial state. The reaction formula is as follows:

\[
\text{SO}_3^-\text{H}^+ + \text{K}^+ \rightarrow \text{SO}_3^-\text{K}^+ + \text{H}^+ \quad (5)
\]

According to the previous experimental results, it can be seen that PEGDA-SMP can achieve an excellent removal efficiency of heavy metal ions in a short time. Therefore, if the desorption can be completed in a short time, it will have more application value. As shown in Figure 9, the desorption efficiency reached above 90% after 30 min for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II). The regeneration after desorption can be completed within 60 min. These results confirm that the cycle of adsorption, desorption, and regeneration can be completed within 120–210 min for Ag(I), Cu(II), Ni(II),
Zn(II), and Pb(II), proving that the PEGDA-SMP adsorbent has a practical application value in wastewater treatment.

2.9. Recycling of the Adsorbent. In addition to the excellent adsorption and desorption efficiency of an adsorbent on heavy metal ions, reusability is also a salient characteristic feature of a good adsorbent. If the adsorbent cannot be used multiple times or the adsorption efficiency is reduced drastically in repeated use, it causes secondary environmental pollution and is also costly in industrial use. It can be seen from Table 3 and Figure 10 that the adsorption efficiency of PEGDA-SMP was slightly decreased after each regeneration and reuse cycle; however, compared with the first use, it still maintained a very high adsorption efficiency. At the 10th cycle, the adsorption efficiencies were 87.41, 88.04, 88.11, 88.89, and 90.60% for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II), respectively. This confirms that the PEGDA-SMP adsorbent can be used repeatedly after regeneration, which reduces the waste generation and has a cost-effective application value for wastewater treatment.

2.10. Wastewater Treatment Applications. Generally, after the treatment of the industrial effluent, heavy metal ions remain in the wastewater, and water quality is not at an acceptable limit. Hence, PEGDA-SMP adsorbents were used in the PCB recovery industry to examine whether the water quality can be improved or not. As shown in Table 4, after the typical wastewater treatment process of the PCB recovery industry effluent, heavy metal ions remained at the ppm level. PEGDA-SMP still displayed high removal efficiencies of Ag(I), Cu(II), Ni(II), Zn(II), Pb(II), and Fe(III), achieving 66.82, 89.39, 90.00, 89.32, 92.93, and 88.89% (Figure 11), respectively. Whether the metal ion composition of an actual wastewater sample is more complicated or not, these results confirm that the PEGDA-SMP adsorbent has a practical application value toward industrial wastewater treatment which contains heavy metal ions.

Table 3. Adsorption Efficiencies of the PEGDA-SMP Adsorbent after Each Reaeration Cycle

| cycle | Ag⁺ | Cu²⁺ | Ni²⁺ | Pb²⁺ | Zn²⁺ |
|-------|-----|------|------|------|------|
| 1     | 100 | 100  | 100  | 100  | 100  |
| 2     | 95.17 | 99.00 | 97.39 | 98.59 | 99.24 |
| 3     | 92.31 | 98.35 | 96.51 | 96.90 | 97.95 |
| 4     | 95.70 | 96.51 | 92.63 | 99.23 | 95.74 |
| 5     | 94.70 | 94.79 | 91.06 | 98.22 | 90.04 |
| 6     | 92.99 | 95.70 | 91.16 | 95.89 | 92.63 |
| 7     | 90.70 | 94.61 | 90.21 | 95.67 | 91.87 |
| 8     | 88.41 | 91.51 | 90.03 | 94.72 | 91.52 |
| 9     | 89.67 | 90.36 | 86.92 | 90.58 | 89.05 |
| 10    | 87.41 | 88.04 | 88.11 | 88.89 | 90.60 |

Table 4. Analyzed Data for the PCB Recovery Industrial Wastewater Sample

| metal ion | concentration (mg/L) | before adsorption | after adsorption | removal efficiency (%) |
|-----------|-----------------------|-------------------|------------------|------------------------|
| Ag⁺       | 0.221                 | 0.073             | 66.82            |
| Cu²⁺      | 1.650                 | 0.175             | 89.39            |
| Ni²⁺      | 0.360                 | 0.036             | 90.00            |
| Pb²⁺      | 0.495                 | 0.035             | 92.93            |
| Fe³⁺      | 0.075                 | 0.008             | 88.89            |
| Zn²⁺      | 0.390                 | 0.042             | 89.32            |

3. CONCLUSIONS

The adsorption of Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II) from an aqueous medium was studied using a PEGDA-SMP
hydrogel adsorbent. The FT-IR spectrums of the modified adsorbent confirmed that the effective modification has occurred. The experimental results indicated that the optimal pH was 5 for all considered heavy metals and it only took 30 min for Cu(II), Ni(II), and Zn(II) but 90 and 120 min for Ag(II) and Pb(II), respectively, to reach adsorption equilibrium. Kinetic data of each metal preferably followed the Langmuir isotherm model. For adsorption efficiencies, when the PEGDA-SMP amount was 10 mg, the removal rate of Pb(II) reached more than 90%, while when the PEGDA-SMP amount was 20 mg, the removal rate of Pb(II) reached more than 90%, while the heavy metal in the aqueous medium after adsorption (mg/L), $V$ = volume of the heavy metal ion solution (L), and $W$ = mass of the adsorbent (g).

To investigate the optimized initial concentration of the adsorbate, adsorption experiments were performed with various initial concentrations from 25 to 300 mg/L.

### 4.5. Emissivity

#### 4.5.1. Emissivity of Heavy Metals

Heavy metal ions, 50 mg of adsorbents was placed in a 10 mL aqueous medium containing 100 mg/L of Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II), respectively, to reach adsorption equilibrium. Kinetic data of each metal preferably followed the Langmuir isotherm model. For adsorption efficiencies, when the PEGDA-SMP amount was 10 mg, the removal rate of Pb(II) reached more than 90%, while when the PEGDA-SMP amount was 20 mg, the removal rate of Pb(II) reached more than 90%. The desorption efficiency reached above 90% after 30 min for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II) with the HNO3 desorber. The regeneration after desorption can be completed within 60 min. These results confirm that the cycle of adsorption, desorption, and regeneration can be completed within 120–210 min for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II), proving that the PEGDA-SMP adsorbent has a practical application value. The adsorption efficiency of PEGDA-SMP was slightly decreased after each regeneration and reuse cycle; however, compared with the first use, it still maintained a very high adsorption efficiency. At the 10th reuse cycle, the adsorption efficiencies were 87.41, 88.04, 88.11, 88.89, and 90.60% for Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II), respectively. This confirms that the PEGDA-SMP adsorbent can be used repeatedly about 10 times after regeneration, which reduces the waste generation and has a cost-effective application value for industrial wastewater treatment.

| metal      | adsorbent                  | adsorption capacity (mg/g) | reference |
|------------|----------------------------|---------------------------|-----------|
| Cu         | commercial Zeolite 4A      | 53.4                      | 33        |
|            | clinoptilolite             | 22.7                      | 33        |
|            | spent-activated clay       | 10.9                      | 33        |
|            | PEGDA-SMP hydrogel         | 99.01                     | this study|
| Ni         | natural zeolite            | 8.69                      | 34        |
|            | citrus limettioides peel   | 35.54                     | 34        |
|            | carbon Escherichia coli    | 13                        | 34        |
|            | PEGDA-SMP hydrogel         | 102.04                    | this study|
| Ag         | MnO2-AG                    | 67.80                     | 35        |
|            | clinoptilolite             | 33.2                      | 35        |
|            | rice husk                  | 1.62                      | 35        |
|            | PEGDA-SMP hydrogel         | 227.27                    | this study|
| Zn         | calcined phosphate         | 23.7                      | 33        |
|            | commercial zeolite 4A      | 31.5                      | 33        |
|            | PEGDA-SMP hydrogel         | 117.64                    | this study|
| Pb         | clinoptilolite             | 26.8                      | 33        |
|            | polystyrene-alumina-activated carbon | 22.47 | 35        |
|            | chitosan-modified biochars | 14.3                      | 35        |
|            | PEGDA-SMP hydrogel         | 263.16                    | this study|

### 4.6. Adsorption Kinetics and Thermodynamics

The contact time on Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II) adsorbents for heavy metal ion concentrations were determined using ICP-OES. The adsorption capacity of the PEGDA-SMP adsorbent for each metal ion was calculated by the following equation

$$Q_e = \frac{(C_0 - C_f)V}{W}$$

where $Q_e$ = equilibrium adsorption capacity of the synthesized adsorbent (mg/g), $C_0$ = initial concentration of the heavy metal in the aqueous medium (mg/L), $C_f$ = concentration of the heavy metal in the aqueous medium after adsorption (mg/L), $V$ = volume of the heavy metal ion solution (L), and $W$ = mass of the adsorbent (g).

To investigate the optimized initial concentration of the adsorbate, adsorption experiments were performed with various initial concentrations from 25 to 300 mg/L.

### 4.7. Effect of pH

The pH of heavy metal solutions was changed from 0 to 5. The desired pH values were adjusted using 0.1 M HNO3 or 0.1 M NaOH solutions, and then, all centrifuge tubes were shaken with a speed of 110 rpm for 24 h at 25 °C. Next, the supernatant of each tube was taken out, and the heavy metal ion concentrations were determined using ICP-OES. Finally, the adsorption capacities at each pH level were calculated according to eq 6.
adsorption onto PEGDA-SMP was determined by reacting 500 mL of 100 mg/L heavy metal ion solutions with 250 mg of the adsorbent in a 500 mL flask. The pH of each solution was adjusted to pH 5; flasks were subjected to magnetic stirring at 110 rpm at 25 °C, and the supernatant was taken out with the time intervals of 30, 60, 90, 120, and 150 min. To evaluate the adsorption control mechanism and potential rate-controlling steps of Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II) ions on PEGDA-SMP, the pseudo-first-order and pseudo-second-order kinetic models were employed fitting the experimental data. The linear forms of the pseudo-first-order and pseudo-second-order equations could be indicated as eqs 7 and 8, respectively,

\[ \ln(Q_e - Q_t) = ln Q_e - k_1t \]  
(7)

\[ \frac{t}{Q_t} = \frac{1}{K_2 Q_e} + \frac{1}{Q_e} \]  
(8)

where \( Q_e \) (mg/g) is the equilibrium adsorption capacity of heavy metal ions, \( Q_t \) (mg/g) is the amount of the adsorbed heavy metal ion at adsorption time \( t \) (min), and \( k_1 \) (min\(^{-1}\)) and \( k_2 \) (g/mg min) are the rate constants of the pseudo-first-order and the pseudo-second-order, respectively.\(^7,21\)

The activation energies for heavy metal adsorption onto the PEGDA-SMP hydrogel were calculated by using the Arrhenius equation, which is indicated as eq 9

\[ k_2 = k_0 \exp\left(-\frac{E_a}{RT}\right) \]  
(9)

The equation can be linearized by taking logarithms as shown in eq 10

\[ \ln k_2 = \ln k_0 - \frac{E_a}{RT} \]  
(10)

where \( k_2 \) (g/mg min) is the rate constant of the pseudo-second-order adsorption kinetic at temperature \( T(K) \), \( k_0 \) (g/mg min) is the frequency factor, \( R \) is the universal gas constant (8.314 J K\(^{-1}\) mol\(^{-1}\)), and \( E_a \) (kJ mol\(^{-1}\)) is the activation energy of the adsorption reaction.\(^36\)

Adsorption experiments were run at 25, 35, 45, 55, and 65 °C to investigate the effect of temperature, with reaction of 500 mL of 100 mg/L heavy metal ion solutions with 250 mg of the adsorbent. The pH of each solution was adjusted to pH 5, and flasks were subjected to magnetic stirring at 110 rpm.\(^36\)

4.7. Adsorption Isotherm Models. Freundlich and Langmuir models were applied to obtained experimental results to interpret the adsorption mechanism. Equation 11 indicates the linearized form of the Langmuir isotherm: \(^7,21\)

\[ \frac{C_e}{Q_e} = \frac{1}{Q_{max} K_l} + \frac{C_e}{Q_{max}} \]  
(11)

where \( Q_{max} \) (mmol g\(^{-1}\)) is the maximum adsorption capacity of the heavy metal; \( C_e \) (mmol L\(^{-1}\)) is the equilibrium concentration of Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II); \( Q_l \) (mmol g\(^{-1}\)) is the equilibrium adsorption of Ag(I), Cu(II), Ni(II), Zn(II), and Pd(II) ions; and \( K_l \) (g mmol\(^{-1}\)) is the Langmuir constant. The degree of suitability of the resin toward heavy metals was estimated from the data of the separation factor constant \( (R_s) \), which was obtained from the following equation (eq 12), where \( K_l \) is the Langmuir equilibrium constant (1/mmol) and \( C_0 \) is the initial concentration of each metal ion (mmol/L)

\[ R_s = \frac{1}{1 + (1 + C_0 K_l)} \]  
(12)

Equation 13 indicates the linearized form of the Freundlich isotherm model and its logarithmic form: \(^7,21\)

\[ \ln Q_e = \ln K_f + \frac{1}{n} \ln C_e \]  
(13)

where \( K_f \) (mmol g\(^{-1}\)) is an indicative constant related to the adsorption capacity of the adsorbent (PEGDA-SMP) and \( 1/n \) (0–1) is the adsorption intensity or surface heterogeneity of the adsorbent PEGDA-SMP.\(^7,21\)

4.8. Desorption Equilibrium Time, Regeneration, and Recycle. 0.5, 1, 2, and 4 M of HNO\(_3\) solutions were prepared as desorbents, and 10 mg of spent PEGDA-SMP adsorbents was put into 200 mL of prepared desorbent solutions. Then, these samples were shaken at 110 rpm for 24 h at 25 °C. Next, 10 mL of the supernatant was taken out at fixed time intervals, and the concentrations of Ag(I), Cu(II), Ni(II), Zn(II), and Pb(II) in the desorbent from ICP-OES were analyzed to determine the desorption equilibrium time. The adsorption process was repeated by the regenerated adsorbent to determine the adsorption efficiencies of each metal in each repeated use.

4.9. Wastewater Treatment Applications. The waste electrolyte sample was taken from the PCB recovery industry, and the silver–palladium alloy ingot was recovered after the pretreatment step of the electrolytic sample. After deteriorating the electrolyte, saturated NaCl was added to react with Ag(I) ions and the AgCl precipitate was formed. Next, the precipitated AgCl was removed from the electrolyte, and the pH of the electrolyte was adjusted between 10 and 11 with NaOH. After flocculation of metal hydroxide, plate and frame filters were used to separate metal hydroxide and the electrolytic solution. Then, the remaining heavy metal concentrations in the electrolyte were determined by ICP-OES. After that, 10 mL of electrolytes was mixed with 50 mg of the PEGDA-SMP adsorbent and reacted with pH 5 under a 110 rpm shaking speed at 25 °C for 24 h. Finally, the supernatant of the electrolyte was analyzed using ICP-OES to determine the remaining metal ion concentrations.

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**Notes**

The authors declare no competing financial interest.
ACKNOWLEDGMENTS

This work was supported by the Ministry of Science and Technology under project MOST 107-2218-E-110-018-MY3 and 110-2221-E-110-024.

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