

Article

Remediation of Heavy Metal Pollution from Coal Mine Effluent Using Metal-Organic Frameworks (MOF): Impact of Water Media, Operational Factors and Metal Characteristics

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Abstract: The energy sector is the sector that generates the highest amount of environmental contamination, especially in water sources, mostly in the case of coal-based energy production. The aim of this study was to examine a significant contamination source, heavy metal contamination, in coal mining effluents. The current investigation introduces an MOF platform based on zirconium clusters and isophthalic acid with NH₂-MIP-SO₃H mixed amine and sulfonic acid functional groups in order to remove the most common heavy metal ions in coal mining effluents, including Hg, Cd, Pb, and Cu ions. The water matrix and the operational conditions were identified to be very influential in the removal process, such as the pH of water, the initial metal concentration and operating time. NH₂-MIP-SO₃H offers a great removal efficiency of metals starting from 745.83 mg/g for Cd, 673.67 mg/g for Cu, 589.85 mg/g for Hg, and 481.66 mg/g for Pb ions, with the Langmuir equation for equilibrium and pseudo-second-order equation for kinetics being the ideal models to express the equilibrium and kinetic data, respectively. A significant impact of water pH was found to occur, with the NH₂-MIP-SO₃H platform performing best at pH 6. Reuse of NH₂-MIP-SO₃H demonstrates excellent reusability, sustaining 90% of initial performance over eight regeneration cycles. The interaction of functional group-functional metal was the dominant mechanism in the removal process. The NH₂-MIP-SO₃H unique approach to heavy metal removal provides a very hopeful outlook for additional investigations in larger-scale studies.

Keywords: coal mining effluent; adsorption; mixed ligand functionalization; heavy metal removal; metal-organic frameworks



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1. Introduction

In recent years, coal is still one of the main resources for electricity generation, particularly for low-income countries, which includes a large portion of energy generated by coal-based technologies, despite the rise in energy technologies and the transition to renewable energies [1–3]. Coal is also considered as a critical material for industries such as cement and steelmaking [4]. Coal mining, which is a critical operation in coal-based energy production, creates effluents consisting of high loads of heavy metals, calcium carbonate, total suspended solids (TSS), and total dissolve solids (TDS) [5]. Heavy metals, as a significant fraction of coal mine effluents, found not only in tailings but also in excavated debris and waste rocks, have been recognized as some of the most important water contaminants since they are not susceptible to biodegradation and tend to accumulate in soil, water, and organisms when they find their way into water bodies [5–7]. The presence of these metals in surface waters creates dangerous effects for local individuals and other organisms [8,9].

The most significant metals in coal mining effluents include Hg, Cd, Cu, and Pb, which may well cause a variety of non-carcinogenic and carcinogenic health problems for humans [10].

While numerous techniques have been developed to remove pollutants from water such as sludge flocculation [11], solvent extraction [12], carbon accounting method [13], membrane filtration [14], and adsorption [15], methods like membrane filtration or solvent extraction face challenges for industrial applications due to either the generation of a concentrated effluent requiring further treatment or the associated high cost of operation and implementation [16]. Adsorption, on the other hand, has fewer drawbacks compared to these other methods and is more straightforward to execute [17]. Additionally, with regards to the majority of heavy metals, the adsorbent would be reusable, as the regeneration of adsorbents only requires a simple desorption process using alcohols or alkali hydroxides [18].

The required characteristics for materials being used for the real-life heavy metal removal include large surface area, porosity, chemical and water stability. These characteristics can be realized in nano-sized materials such as graphene [19], metal-organic frameworks (MOFs) [20], magnetic nanoparticles [21], and biosorbents [22]. In these materials, MOFs can be used to remove heavy metals from liquid environments, and MOFs, a group of metal ions linked by organic connections, can be used to create large, clean surfaces with appropriate system function ability and open framework [23]. According to the writer, MOFs can have chelation of heavy metals or electrostatic interaction at the surface for the capture of heavy metals from a liquid environment [24].

Functional groups incorporating S-, N-, and Cl- atoms have shown greater affinities for the capture of Hg, Cd, Cu, and Pb present in coal mining effluents. For instance, The modification of biochar with amine-containing functional groups exhibited five times greater capacity for copper ions compared to unmodified biochar [25]. Modification $\text{Fe}_3\text{O}_4@\text{C}$ nanoparticle with carboxyl and sulfonate groups had a high removal efficiency (>90%) of Hg, Pb, and Cd ions [26]. A copper hydroxyl salts@MOF study was also functionalized with SH-containing groups, and an efficiency of 626.6 mg/g was reached for Hg ions removal from water [27]. The investigation discovered that the affinity of Hg ions and SH groups has led to Hg capture by this core-shell structure. Successful removal of Pb ions occurred from Zr-MOFs functionalized with polyethyleneimine, displaying an adsorption capacity of 273.2 mg/g [28]. The study focused on the mechanism by which Pb ions are adsorbed on the MOF, which was additionally studied through FTIR analysis before and after Pb adsorption to discover that N-containing groups were very crucial to the adsorption of Pb ions. With our current understanding of the technology, and despite these advances, there is no study to date that reports the development of an adsorbent that can simultaneously capture all metals to remediate the metal contamination portion of coal mining wastewater.

In recent years, zirconium-based MOFs are given particular attention for environmental applications [29,30]. Zirconium-based MOFs have found interesting applications because of their excellent chemical and thermal stability, high surface area, and the potential to tailor their surfaces to incorporate different functional groups [31,32]. Zirconium seems to possess exceptional stability in water and even in organic solvents, even more when it is within an MOF [33]. Zirconium is relatively resistant to various stress environments than other operations, making them perfect for operational environments with coal mining effluents [34,35]. It is able to support many bonds with organic linkers to form MOFs with a variety of topologies [36]. With respect to the significant coordination number of zirconium, when we combine IPA, a common linker, with this ion, we can generate an MOF with mixed amines (NH_2) and sulfonic acids (SO_3H). These functional groups create improved chemical and functional options for removing heavy metal ions [37]. They greatly increase heavy metal ion adsorption, as compared to traditional materials where absorption is governed entirely by the surface area and functional moieties. All the new MOFs were demonstrated to have multiple reactive sites for the removal of ions, providing good accessibility of the many reactive sites for hard or soft acid and base interactions with metal ions. The high surface area and reactive sites of this material make the MOF competitive.

The current study aims to create a platform for the simultaneous capture of the most prevalent heavy metals in coal mining effluent, including Hg, Cd, Cu, and Pb ions. For this purpose, a novel MOF consisting of Zr clusters as metal centers bridged with isophthalic acid (IPA) as ligands was designed with a mixed-ligand approach incorporating both NH_2 - and SO_3H -groups to target the mentioned heavy metals. Batch experimental trials were employed to evaluate the process parameters such as metal concentration, water pH, process time, and the recyclability of the adsorbent. Characterization of the synthesized adsorbent was performed by FTIR, XRD, BET, SEM, and TGA. The removal mechanism was determined by isotherm studies and FTIR analysis before and after the adsorption, while kinetic analysis was performed with the process time data by applying kinetic models to the data.

2. Materials and Methods

2.1. Chemicals Reagents

The list of chemicals used in the current study include formic acid (FA; Merck, Shanghai, China), 5-OH-IPA (Sigma Aldrich, Shanghai, China), 5- NH_2 -IPA (Sigma Aldrich), 5- SO_3H -IPA (Sigma Aldrich), zirconium IV oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$; Sigma Aldrich), sodium hydroxide (NaOH; Merck), hydrochloric acid (HCl; Merck), lead nitrate ($\text{Pb}(\text{NO}_3)_2$; Shanghai Macklin Biochemical Co., Ltd., Shanghai, China), copper nitrate ($\text{Cu}(\text{NO}_3)_2$; Shanghai Macklin Biochemical Co., Ltd.), cadmium nitrate ($\text{Cd}(\text{NO}_3)_2$; Shanghai Macklin Biochemical Co., Ltd.), and mercury nitrate ($\text{Hg}(\text{NO}_3)_2$; Shanghai Macklin Biochemical Co., Ltd.). A synthetic mine wastewater was prepared by dissolving heavy metal salts in pure water to be used in adsorption experiments. A water sample was taken from a real coal-mining site (Huolinhe Coal Mine; Huolinhe, Holingol, Tongliao, Inner Mongolia, China) to assess the application of the adsorbent in the treatment of real water samples.

2.2. Synthesis Procedure

The procedure introduced by Wang et al. was used in this study with modifications [38]. Firstly, 7.28 g 5-OH-IPA, 3.62 g 5- NH_2 -IPA, and 3.58 g 5- SO_3H -IPA were mixed with 38.6 g $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 100 mL FA. The mixture was transferred to a Teflon reactor, then the temperature was increased to 200 °C and kept for 24 h. Next, the temperature of the reactor was decreased to 25 °C to stop the reaction. The final solid product was separated from the solvent and unreacted chemicals, and it was washed with acetone and hot water to remove impurities. The material was dried in an oven at 80 °C for 12 h, named $\text{NH}_2\text{-MIP-SO}_3\text{H}$, and stored at room temperature for further use. The schematic illustration of the synthesis and the pore structure of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ is presented in Figure 1.

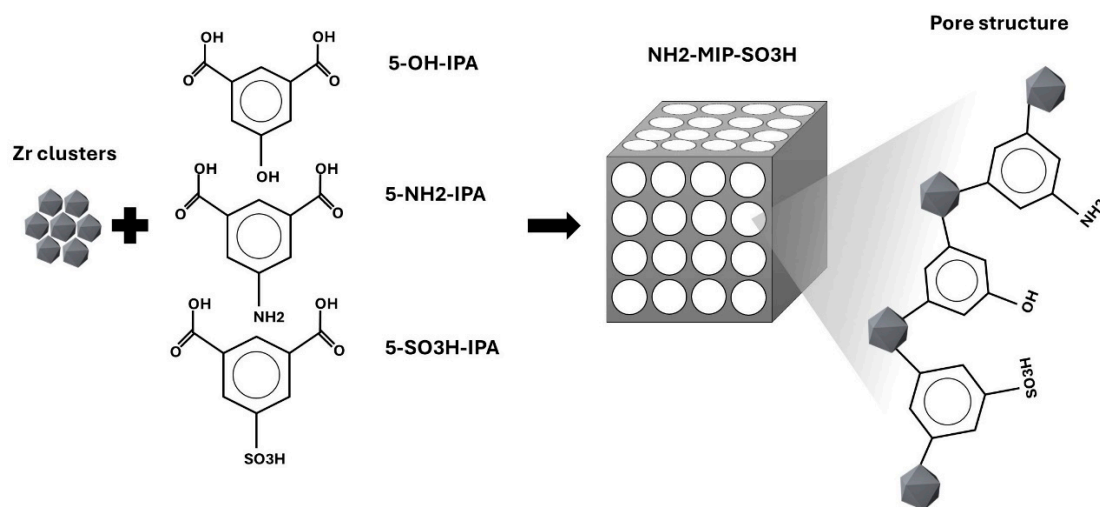


Figure 1. Schematic illustration of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ synthesis and its pore structure.

2.3. Instruments

The FTIR technique was utilized to define functional groups in the adsorbent as well as to examine the metal removal mechanism. FTIR spectroscopy analyses were conducted using Thermoscientific Nicolet iS50 (Thermo Fisher Scientific Inc., Waltham, MA, USA) and its attenuated total reflectance (ATR) accessory. The surface area accessible in NH₂-MIP-SO₃H was determined using the gas adsorption analyzer, Micromeritics TriStar II (Micromeritics Instrument Corporation, Norcross, GA, USA), according to the BET model. The XRD method was performed to analyze the crystallinity of NH₂-MIP-SO₃H via a diffractometer model Bruker D8 Advance (Bruker Corporation, Billerica, MA, USA). The electron microscope images of the adsorbent were taken using a Zeiss Leo Supra 35 VP FEG SEM (Carl Zeiss Microscopy GmbH, Oberkochen, Germany). The thermal stability of NH₂-MIP-SO₃H was analyzed using a NETZSCH JUPITER STA 449 instrument (NETZSCH-Gerätebau GmbH, Selb, Germany). The ¹H NMR spectra of materials dispersed in a D₂O/KOH mixture were obtained using a Bruker Avance 300 spectrometer (Bruker BioSpin GmbH, Rheinstetten, Germany).

2.4. Heavy Metal Removal Procedure

An experimental setup in a batch mode was conducted to study the heavy metal removal properties of NH₂-MIP-SO₃H. For this purpose, a 50 mg NH₂-MIP-SO₃H was put in 100 mL metal-contained water samples with concentrations of 5–500 mg/L. The samples were stirred for 24 h to reach the absorption equilibrium stage. Subsequently, NH₂-MIP-SO₃H particles were separated by filtration, and residual metal in the solution was detected by ICP-MS. Thus, the removal capacity was calculated by subtracting the metal content before and after the process by using Equation (1). For multi-metal samples, the process parameters were 50 mg of NH₂-MIP-SO₃H, and 100 mL water samples with a total metal concentration range of 5–500 mg/L while each metal contributed 25% of the total metal content.

$$Q_e = (C_i - C_e) \times \frac{V}{m} \quad (1)$$

where, Q_e (mg/g) is the metal removal capacity of NH₂-MIP-SO₃H, C_i (mg/L) is the metal content before the process, C_e (mg/L) is the metal content after the process, m (g) and V (L) are the mass of NH₂-MIP-SO₃H and water volume, respectively.

The analysis of the process time was performed with similar batch mode experiments as mentioned earlier. Typically, 50 mg of NH₂-MIP-SO₃H was introduced to 100 mL water samples at a metal concentration of 500 mg/L. The samples were maintained under stirring conditions for different time intervals in the range of 1–180 min. The residual metal content was measured utilizing ICP-MS. The removal capacity was calculated using Equation (1). Furthermore, the process parameters for the analysis of water pH were 50 mg NH₂-MIP-SO₃H, and 100 mL of water samples with metal concentration of 100 mg/L, at different pH of 2–12. The samples were stirred for 24 h to reach equilibrium. The removal capacity was calculated using Equation (1).

The recycling potential of NH₂-MIP-SO₃H for the removal of heavy metals was investigated by performing several adsorption-desorption steps. For the desorption of the adsorbate, the used adsorbent was immersed in excess 0.5 M NaOH and kept at that level for a whole day. Next, they were washed with water, dried, and then used for the next adsorption process.

3. Result and Discussion

3.1. Characterization

XRD results of NH₂-MIP-SO₃H show that the material has a crystalline structure, which is confirmed by the SEM images (Figure 2C). There were characteristic peaks at 10°, 9.2°, 8°, 7.2°, 6.1°, 5.9°, 5.3°, and 3.3°, in agreement with those reported in the literature for pristine MIP-206 [38]. This indicates that the functionalization of NH₂-MIP-SO₃H is nondisruptive to the MOF structure.

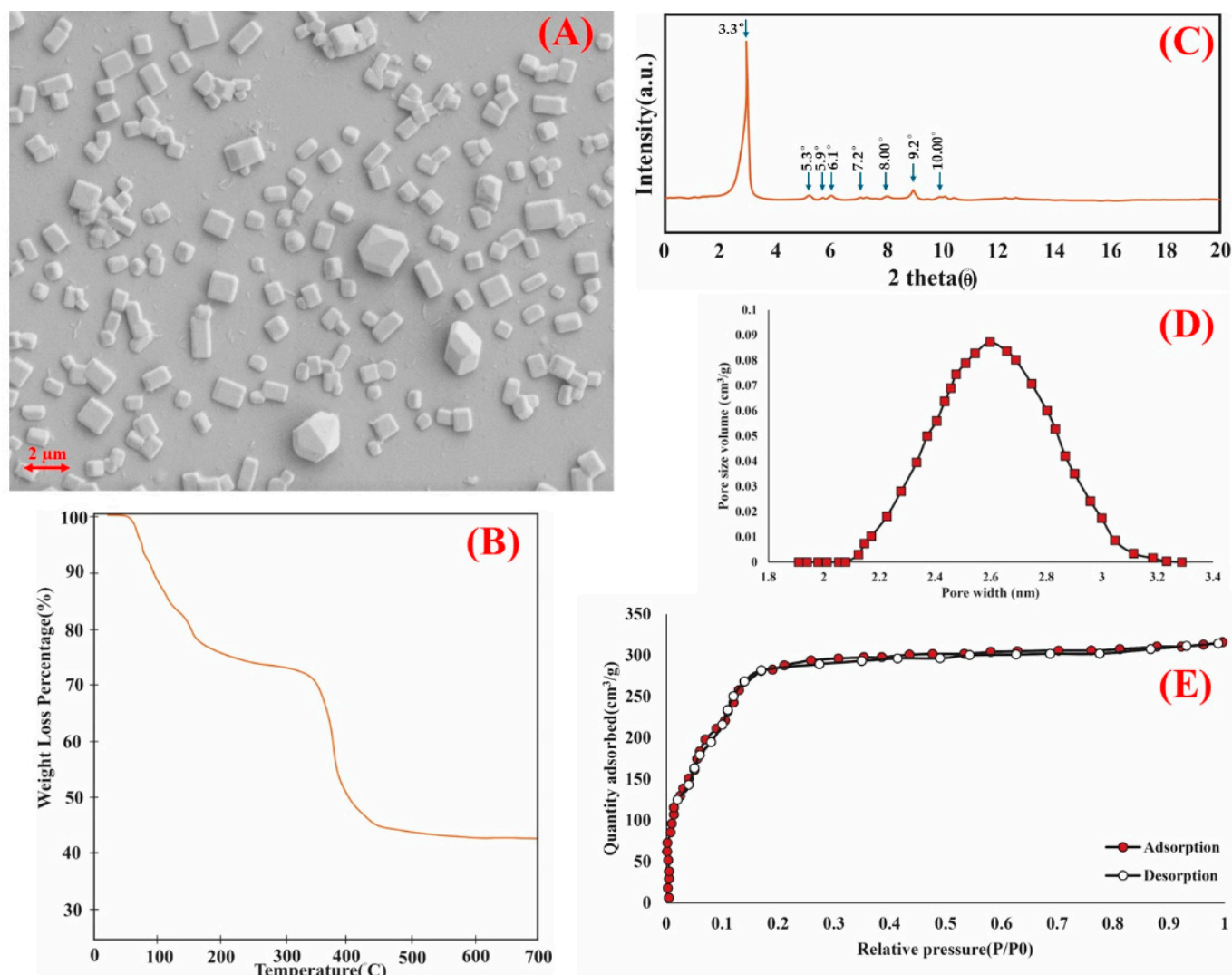


Figure 2. (A) SEM image of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ at EHT of 3.00 kV, WD of 8.6 mm and magnification of 30 KX, (B) TGA analysis of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ in the temperature range of 0–700 °C, (C) XRD analysis of $\text{NH}_2\text{-MIP-SO}_3\text{H}$, (D) pore size distribution of $\text{NH}_2\text{-MIP-SO}_3\text{H}$, and (E) nitrogen adsorption-desorption isotherms of $\text{NH}_2\text{-MIP-SO}_3\text{H}$.

The SEM image of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ is shown in Figure 2A. The crystal of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was mainly cubic in structure and some have hexagonal shapes. Some particles with different shapes may represent impurities or incomplete crystallization, due to local variations in the synthesis environment or mechanical mixtures of phases not fully integrating into the primary MOF structure during the synthesis process. The surface of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ is smooth, while most of the particles were in the range of 1–2 μm .

TGA of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was presented in Figure 2B. TGA results displayed two major weight losses at 100–260 °C and 320–460 °C. The first weight loss may be attributed to desorption of entrapped water and solvent, decarboxylation of formates, and cleavage of side chains. There are amine and sulfonic acid groups in the polymer that would likely decompose into amine and sulfonic acid derivatives. The second step involved the decomposition of the ligand and MOF structure between 320 and 460 °C, and the full conversion of the MOF crystals and loss of crystallinity will likely take place in this step, and the remaining mass corresponded to ZrO_2 .

In Figure 2D,E, the pore size distribution and N_2 adsorption-desorption isotherms of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ are displayed. The N_2 adsorption-desorption isotherm of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ confirms that the material has a mesoporous pore structure. From the N_2 adsorption-

desorption isotherm, we can see that it shows type IV isotherm behavior. $\text{NH}_2\text{-MIP-SO}_3\text{H}$ has a surface area calculated to be $1153.4 \text{ m}^2/\text{g}$, and total pore volume of $0.459 \text{ cm}^3/\text{g}$. The high surface area and volume shows that $\text{NH}_2\text{-MIP-SO}_3\text{H}$ is a promising material for water treatment applications, because it can remove many contaminants. The pore size distribution of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ implies a good mesopore network, where the pore size is about 2.6 nm.

The ^1H NMR result for $\text{NH}_2\text{-MIP-SO}_3\text{H}$ is depicted in Figure 3. The obtained signals illustrate the protons in between carboxylic moieties and adjacent to functional groups such as $-\text{OH}$, $-\text{NH}_2$, and $-\text{SO}_3\text{H}$. The signal corresponding to a specific location in the structure of ligands is identified by alphabetic letters. For example, the signal at 7.6 ppm (identified as c) is attributed to the protons in between carboxylic groups and the signal at 7.2 ppm is attributed to the protons adjacent to $-\text{SO}_3\text{H}$ groups in 5- $\text{NH}_2\text{-IPA}$. Therefore, the formation of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was confirmed using ^1H NMR analysis as signals regarding all three ligands (5- OH-IPA , 5- $\text{SO}_3\text{H-IPA}$, 5- $\text{NH}_2\text{-IPA}$) were present in the ^1H NMR spectra. The composition of ligands was also calculated from ^1H NMR spectra. It was observed that the ligand ratios were comparable to the experimental input percentages. Specifically, the ligand ratios obtained from ^1H NMR were molar percentages of 52.32%, 25.84%, and 21.82% for 5- OH-IPA , 5- $\text{SO}_3\text{H-IPA}$, and 5- $\text{NH}_2\text{-IPA}$, respectively, while the experimental input molar ratios were 50%, 25%, and 25% for 5- OH-IPA , 5- $\text{SO}_3\text{H-IPA}$, and 5- $\text{NH}_2\text{-IPA}$, respectively. This slight difference might be due to the affinity difference of ligands and the synthesis process.

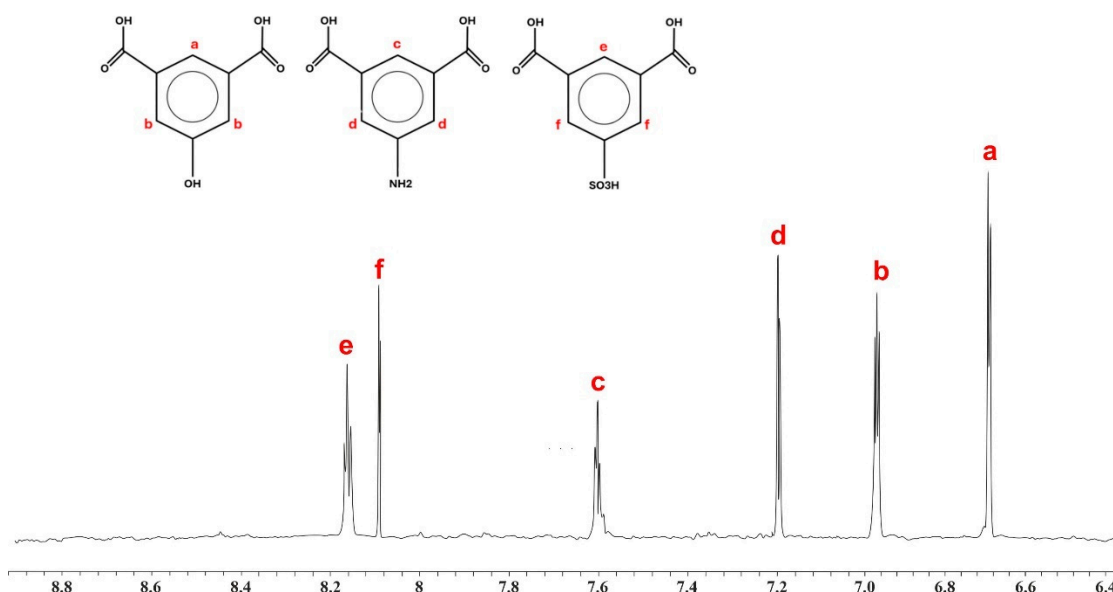


Figure 3. ^1H NMR spectra of $\text{NH}_2\text{-MIP-SO}_3\text{H}$.

The FTIR analysis of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ before and after the removal of metal is given by Figure 4. The $\text{NH}_2\text{-MIP-SO}_3\text{H}$ used before the removal of metal exhibited peaks at 1720 and 1620 cm^{-1} , which can be assigned to the $\text{C}=\text{C}$ bonds related to aromatic compounds [39]. Around 1545 cm^{-1} originated from the $\text{C}-\text{C}$ bond, and around 1459 cm^{-1} from $\text{C}-\text{H}$ bonds. The amine groups could be noticed by the peaks around $3300\text{--}3500 \text{ cm}^{-1}$ and the band around 1630 cm^{-1} , which both can be assigned to the $\text{N}-\text{H}$ bonds [40]. Additional AM bands showing the presence of an amine group were around 1345 and 1092 cm^{-1} , which can be assigned to the $\text{C}-\text{N}$ bond [41]. Also needed to be pointed out were the prominent bands related to the existence of the sulfonic acid groups about 1137 and 1040 cm^{-1} .

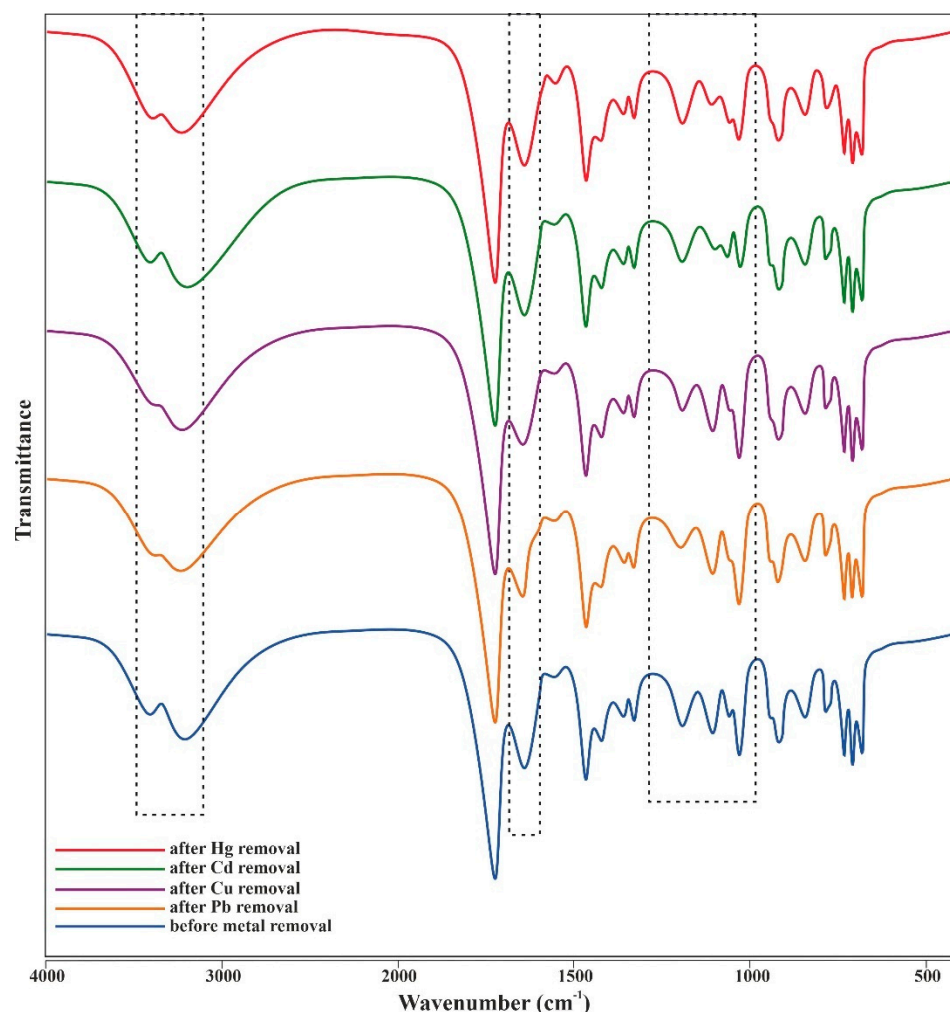


Figure 4. FTIR spectra of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ before and after metal removal process.

After the metal removal process, some changes in peak intensities related to amine and sulfonic acid groups were observed. Particularly, the interaction between Hg and Cd ions with sulfonic acid groups and the interaction between Cu and Pb ions with amine groups were more distinct. The major change was observed in the FTIR spectra of the $\text{NH}_2\text{-MIP-SO}_3\text{H}$ after the removal of Hg and Cd with intensity reduction of the peak at 1137 and 1040 cm^{-1} , with also a minor decrease in intensity of the amine peak such as 1345 cm^{-1} and a peak around $3300\text{--}3500\text{ cm}^{-1}$. Conversely, the FTIR spectra of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ after Cu and Pb removal showed a decrease in peak intensities mostly of amine groups, with some slight changes in the intensity of sulfonic acid group peaks. Therefore, the mechanism of metal removal was identified as the coordinative interaction of specific functional groups with metals.

3.2. Adsorption Experiments

Due to the metal speciation at different pHs and variations in the surface charge of the adsorbent, investigating the impact of pH holds significant importance. Therefore, the impact of water pH was investigated in the range of 2–12 (Figure 5). Figure 5 illustrates the general increasing trend in removal capacities at low pHs (2–6) and then the decreasing trend at higher pHs (6–12). The highest removal capacities for Hg^{2+} , Pb^{2+} , Cd^{2+} , and Cu^{2+} were achieved at pH 6, which was considered the optimal pH for the rest of the study. The lower removal capacities at pH below 6 can be interpreted by the competition between hydrogen and metal ions to be adsorbed on the active sites of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ [42]. Due to the excess number of hydrogen ions, they were preferentially captured by the

active sites on the surface of $\text{NH}_2\text{-MIP-SO}_3\text{H}$. Meanwhile, the point of zero charge (pH_{PZC}) for $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was measured to be 5.2, indicating that at $\text{pH} < \text{pH}_{\text{PZC}}$, the surface charge of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was positive [43]. This further contributed to decreasing the metal removal capacity due to the repulsive electrostatic forces between the surface of the adsorbent and metal cations. The surface charge of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was negative at $\text{pH} > \text{pH}_{\text{PZC}}$; therefore, the highest metal removal capacity at pH 6 may be attributed to the attractive electrostatic forces between metal cations and the negatively charged surface of $\text{NH}_2\text{-MIP-SO}_3\text{H}$. At basic pHs, the metals being investigated in this research occur as the forms of $\text{M}(\text{OH})^+$, $\text{M}(\text{OH})_2$, and $\text{M}(\text{OH})_3\text{M}(\text{OH})_3^-$ [44,45]. Because of this, it is obvious that the surface of the adsorbent was negatively charged at $\text{pH} > \text{pH}_{\text{PZC}}$; however, the metal as a hydroxide at basic pH forms could not adsorb to the active sites of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ at $\text{pH} > 7$ but implies that the appropriate pH range for removing these metals by $\text{NH}_2\text{-MIP-SO}_3\text{H}$ is 5.2–7, where the maximum adsorption capacities occur at pH 6.

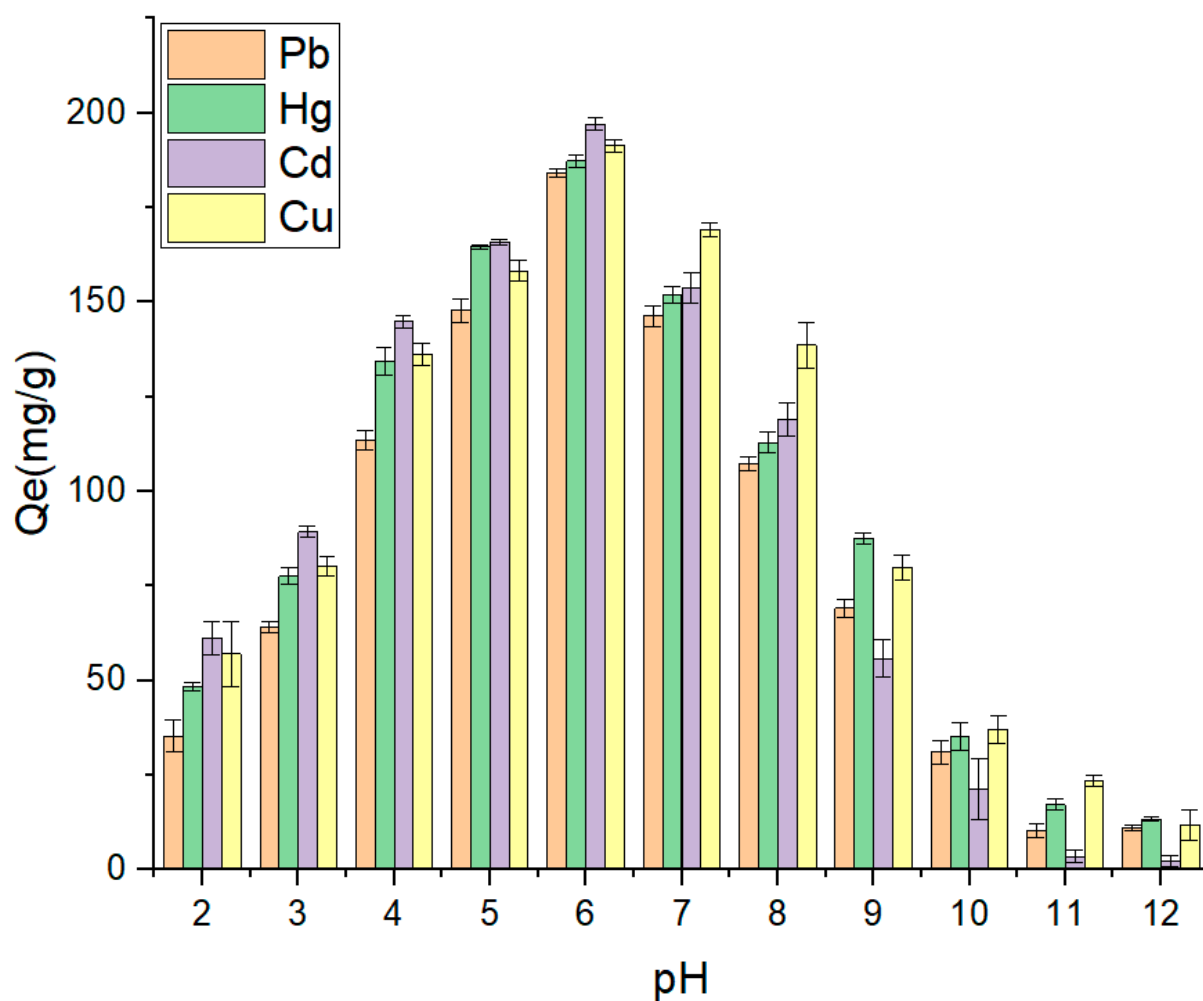


Figure 5. The influence of water pH on heavy metal removal including Hg, Pb, Cd, and Cu over a pH range of 2–12 at metal concentration of 100 mg/L.

The influence of process time on heavy metal removal is presented in Figure 6. The interpretation of the kinetic data was performed by fitting the kinetic data with pseudo-first-order, pseudo-second-order, and Elovich kinetic models (Equations (2)–(4)).

$$Q_e = Q_m \left(1 - e^{-K_1 \times t} \right) \quad (2)$$

$$Q_e = \frac{K_2 \times Q_m^2 \times t}{1 + K_2 \times Q_m \times t} \quad (3)$$

$$Q_e = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln(t) \quad (4)$$

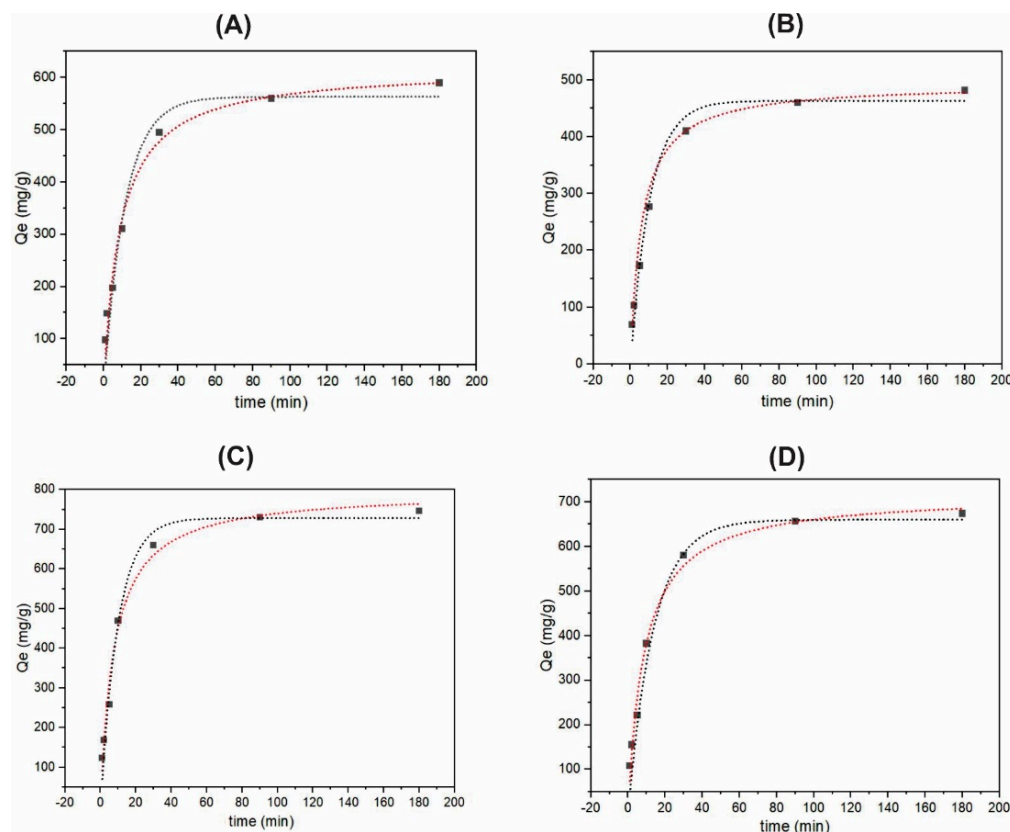


Figure 6. Influence of process time on heavy metal removal at pH 6 and temperature of 25 °C, including (A) Pb, (B) Hg, (C) Cd, and (D) Cu as well as fitting of kinetic models; (red dash lines) pseudo-second order model, and (black dash lines) pseudo-first order model.

Here, Q_e (mg/g) denotes the equilibrium capacity after time t , Q_m (mg/g) denotes the theoretical capacity calculated from the fitting of kinetic models, and K_1 (1/min) and K_2 (g/mg.min) are the constant parameters of the models fitted.

Figure 6 shows that the saturation point of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ for all the metal ions investigated was similar, probably due to similarities in charge and size, achieving equilibrium in the first 90 min. The fitting of kinetic models and the calculated parameters (Table 1) demonstrate that the pseudo-second-order model has better capacity in interpreting the kinetic data than the pseudo-first-order model, as indicated by the correlation coefficients > 0.99 and the closer theoretical capacities to the actual experimental capacities of metal ion removal. Particularly, the theoretical capacities calculated from the fitting of kinetic models were 608.29, 490.3, 776.97, and 707.82 mg/g for Pb, Hg, Cd, and Cu ions, respectively, which have less difference with the actual capacities than those calculated for the pseudo-first-order model. This consistency of data with the pseudo-second-order model revealed that the heavy metal removal process is controlled by chemical interactions with the adsorbent surface rather than physical interactions such as diffusion and size exclusion [46,47].

Table 1. Kinetic parameters for the heavy metal removal process, including Hg, Pb, Cd, and Cu ions.

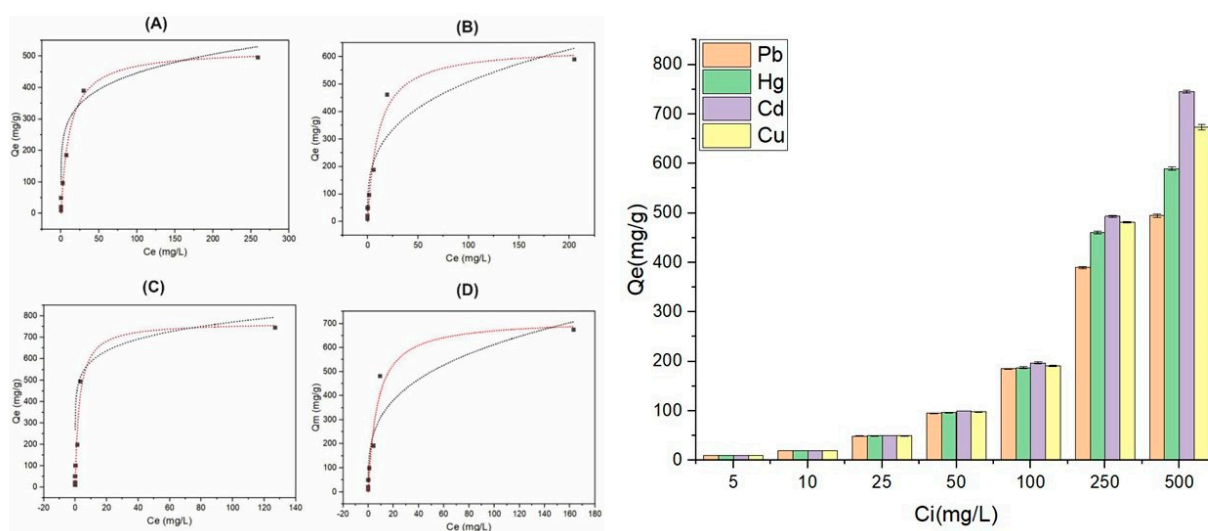
Heavy Metals	Q_m Actual (mg/g)	Pseudo-First Order			Pseudo-Second Order			Elovich		
		Q_m (mg/g)	K_1 (1/min)	R^2	Theoretical Q_m (mg/g)	K_2 (g/mg.min)	R^2	α (mg/g.min)	β	R^2
Pb	482.66	513.23	0.0876	0.964	490.29	0.00017	0.991	389.439	0.0107	0.931
Hg	589.85	433.65	0.0953	0.985	608.37	0.00032	0.993	919.873	0.0157	0.741
Cd	745.83	628.346	0.1012	0.981	776.97	0.00016	0.990	713.218	0.0087	0.924
Cu	673.67	620.077	0.0723	0.946	707.82	0.00016	0.993	468.043	0.0092	0.936

The influence of metal concentrations in a single-metal environment is presented in Figure 7. The enhancement of metal concentration led to an increasing trend in removal capacities, due to the availability of more metals at higher concentrations to be captured by the active sites of NH₂-MIP-SO₃H. Eventually, saturation occurred at the highest metal content. The removal capacity of NH₂-MIP-SO₃H was in the order of Cd > Cu > Hg > Pb. This order suggests that, in addition to the affinity of different moieties with metals, the ligand molar ratios play a role. The high Cd removal capacity might be attributed to the presence of more -SO₃H moieties. Future research could be directed to investigate the ligand ratios to enhance specific interactions and improve selectivity. The equilibrium data was analyzed by isothermal equations, including Langmuir, Freundlich, and Sips (Equations (5)–(7)).

$$Q_e = \frac{C_e K_l Q_m}{1 + C_e K_l} \quad (5)$$

$$Q_e = K_f C_e^{1/n} \quad (6)$$

$$Q_e = \frac{q_s a_s C_e^{1/sp}}{1 + a_s C_e^{1/sp}} \quad (7)$$

**Figure 7.** Influence of metal concentration on the removal capacity of NH₂-MIP-SO₃H at pH 6 and temperature of 25 °C for (A) Pb, (B) Hg, (C) Cd, and (D) Cu ions as well as fitting of isotherms; (red dash lines) Langmuir isotherm, and (black dash lines) Freundlich isotherm.

Here, Q_e (mg/g) represents removal capacity at equilibrium, Q_m (mg/g) represents theoretical capacity calculated from isothermal equations, C_e (mg/L) represents the metal concentration at equilibrium, K_l (L/mg) and K_f (mg/g) denote isothermal parameters of Langmuir and Freundlich equations, respectively.

Isothermal parameters calculated from Langmuir and Freundlich equations (Table 2), such as correlation coefficients, show that the Langmuir equation has better capacity in

predicting the metal removal data. This consistency with the Langmuir equation revealed that all metals were captured in a monolayer manner on energetically equal sites, suggesting that either -NH_2 or $\text{-SO}_3\text{H}$ moieties were responsible for the capture of each metal. The single-metal removal experiments demonstrated that $\text{NH}_2\text{-MIP-SO}_3\text{H}$ exhibited superior performance in heavy metal removal compared to most of the reported materials in the literature [48,49]. Table 3 presents a comparison between the performance of the adsorbent prepared in the current study and some recently reported materials in the literature. The performance of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ in multi-metal mixtures is presented in Figure 8. It was observed that the performance of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ varies significantly when all metals are present in the matrix, as indicated by the large error bars in the figure. This is probably due to the similarity in charge and size of the metal ions, which hinders any selectivity. Additionally, the trend in removal capacities ($\text{Cd} > \text{Cu} > \text{Hg} > \text{Pb}$) observed in single-metal solutions is not observable in multi-metal solutions anymore. For example, $\text{NH}_2\text{-MIP-SO}_3\text{H}$ has similar performance regarding Pb ions in the single-metal solution, 100 mg/L concentration of metal ions, to other metal ions, while in the multi-metal solutions, $\text{NH}_2\text{-MIP-SO}_3\text{H}$ did show selective capabilities, by capturing more Pb ions than Hg and Cu ions.

Table 2. Isothermal parameters for the heavy metal removal process, including Hg, Pb, Cd, and Cu ions.

Heavy Metals Q_m Actual (mg/g)		Langmuir			Freundlich			Sips			
		Q_m (mg/g)	K_l (L/mg)	R^2	n	K_f (mg/g)	R^2	q_s	a_s	sp	R^2
Pb	482.66	527.627	0.086	0.991	3.413	104.23	0.891	495.23	0.0503	0.795	0.989
Hg	589.85	625.54	0.11	0.988	5.18	229.18	0.884	849.26	0.051	1.342	0.953
Cd	745.83	776.05	0.38	0.979	8.403	445.79	0.783	736.75	0.0321	0.844	0.964
Cu	673.67	721.42	0.14	0.975	3.401	158.16	0.873	678.26	0.0493	0.675	0.973

Table 3. Comparison between the performance of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ with recently reported adsorbents for heavy metal removal.

Adsorbent	Investigated Heavy Metal	Maximum Removal Capacity (mg/g)	References
chitosan-pectin gel beads	Cu, Cd, Hg, Pb	169.4, 177.6, 208.5, 266.5	[48]
polyamidoamine dendrimer grafted magnetic graphene oxide nanosheets	Cd, Pb, Cu	435.85, 326.73, 353.59	[49]
fly ash	Pb, Cd	126.55, 56.31	[50]
UiO-66-EDA	Pb, Cd, Cu	243.90, 217.39, 208.33	[51]
Ag-MOF/chitosan composite	Pb, Cu, Cd	372.96, 94.67, 193.34	[52]
$\text{NH}_2\text{-MIP-SO}_3\text{H}$	Pb, Hg, Cd, Cu	482.66, 589.85, 745.83, 673.67	Current study

The feasibility of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ for industrial applications was investigated by performing reusability tests over multiple regeneration cycles (Figure 9). The removal capacities gradually decreased over cycles, probably due to pore blockage or poor desorption of metals from the surface of $\text{NH}_2\text{-MIP-SO}_3\text{H}$, which led to the occupation of active sites for the next cycle [53–55]. Reusability tests of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ enabled its adsorption capacity for Hg and Cu ions to remain stable at approximately 90% for 8 cycles and for Cd and Pb ions for 9 cycles. These results suggest that the $\text{NH}_2\text{-MIP-SO}_3\text{H}$ material performed notably well and that it may show promise towards industrial-scale applications in the near future.

3.3. Applicability in Real Coal-Mining Wastewater

The results of the application of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ for real wastewater treatment from a coal-mining area in China are presented in Table 4. The wastewater sample contains

heavy metals other than the ones investigated in the current study, such as Fe, Cr, and Ni. Regardless of the complex wastewater matrix, $\text{NH}_2\text{-MIP-SO}_3\text{H}$ exhibited satisfactory performance in the treatment of all heavy metals present in the real wastewater sample. After the treatment of the real wastewater sample with $\text{NH}_2\text{-MIP-SO}_3\text{H}$, the concentration of all heavy metals was reduced significantly.

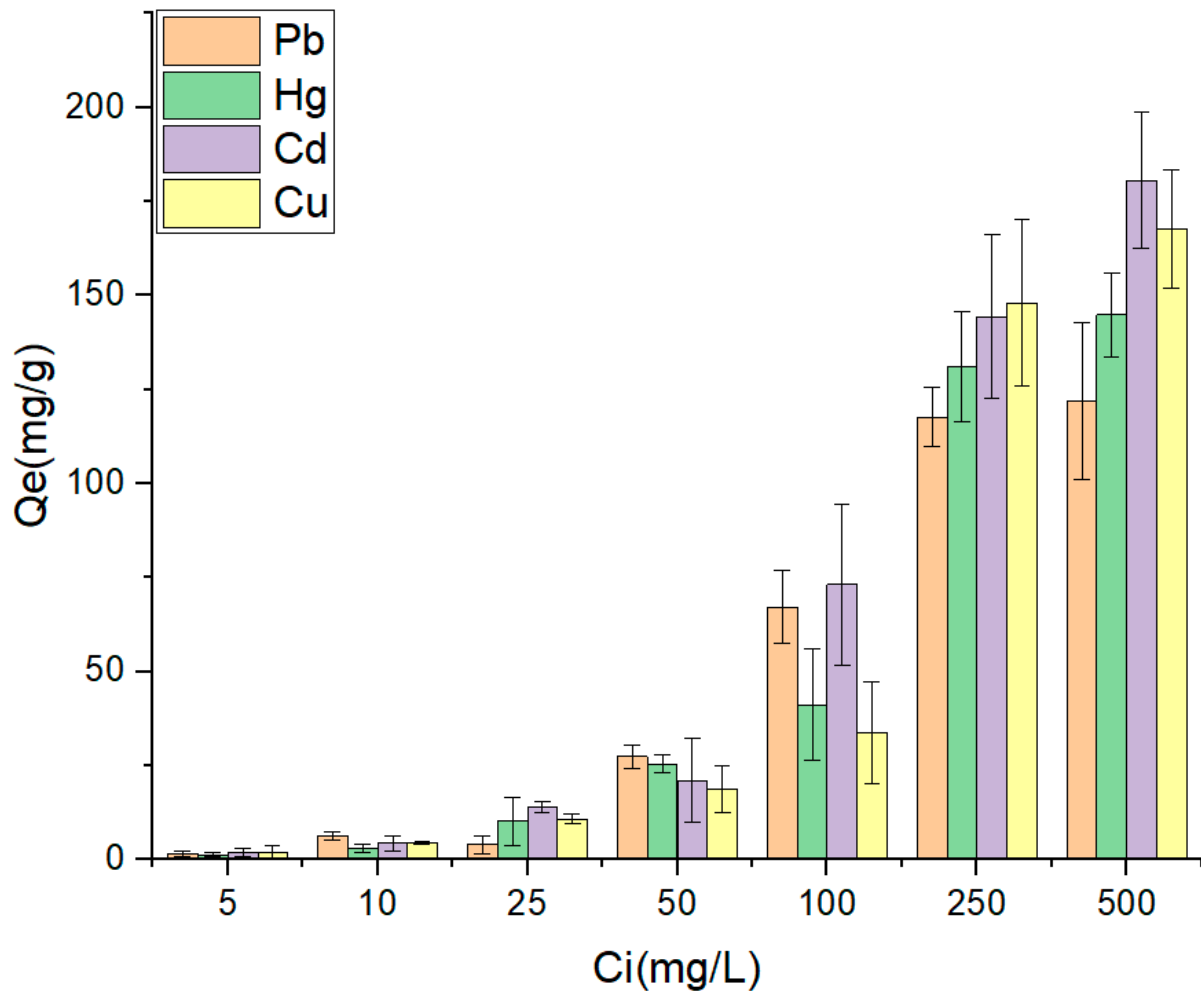


Figure 8. Performance of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ for heavy metal removal at pH 6 and temperature of 25 °C in multi-metal mixtures at different metal concentrations; the concentration of each metal was 25% of the total concentration.

Table 4. Physiochemical properties of real coal-mining wastewater from Huolinhe Coal Mine (Huolinhe, Holingol, Tongliao, Inner Mongolia, China) before and after treatment with $\text{NH}_2\text{-MIP-SO}_3\text{H}$.

Heavy Metal	Heavy Metal Concentration (mg/L) before the Treatment with $\text{NH}_2\text{-MIP-SO}_3\text{H}$	Heavy Metal Concentration (mg/L) after the Treatment with $\text{NH}_2\text{-MIP-SO}_3\text{H}$
Pb	4.912	0.005
Hg	3.699	0.003
Fe	0.485	0.090
Cr	0.225	0.019
Cd	5.810	0.011
Cu	5.353	0.008
Ni	0.091	0.001

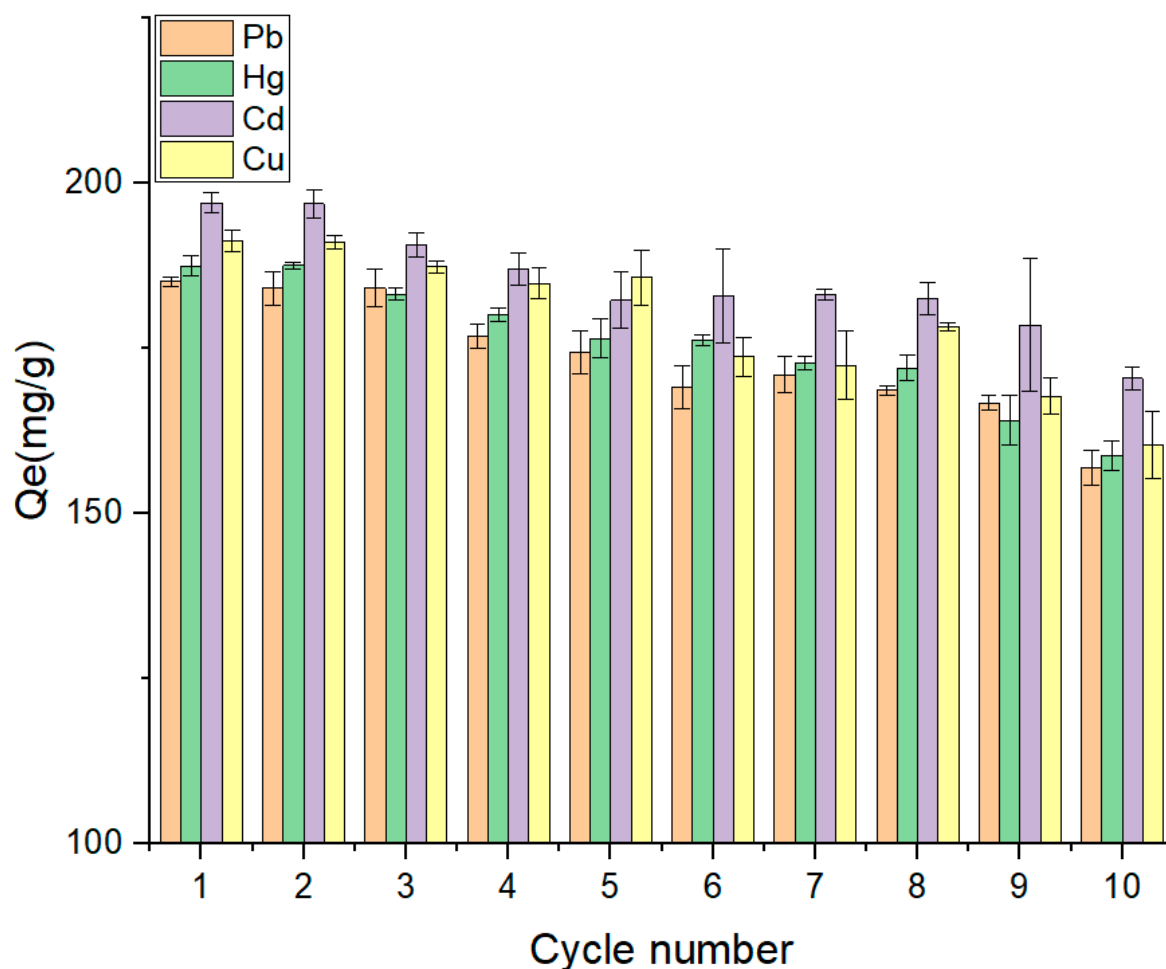


Figure 9. Reusability performance of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ over 10 regeneration cycles; all experiments performed at pH 6, temperature of 25 °C, and metal concentration of 100 mg/L.

4. Conclusions

In summary, with amine and sulfonic acid ligands integrated into a new mixed ligand approach, $\text{NH}_2\text{-MIP-SO}_3\text{H}$ performed extraordinarily well in removing the four most common heavy metals in coalmining effluents, including Hg, Cd, Pb, and Cu. The adsorption equilibrium data of the metals by $\text{NH}_2\text{-MIP-SO}_3\text{H}$ fitted the Langmuir isotherm model and the adsorption process data were best fitted by the second-order kinetic model. $\text{NH}_2\text{-MIP-SO}_3\text{H}$ exhibited the highest adsorption capacities for Cd, Cu, Hg, and Pb as 745.83 mg/g, 673.67 mg/g, 589.85 mg/g, and 481.66 mg/g, respectively. All four metal ions were notably removed from different synthetic samples at different amounts. The best performance of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was found to occur at pH 6; this was as the performance was at a comparable level over a wide pH range. The reusability of $\text{NH}_2\text{-MIP-SO}_3\text{H}$ was observed by using the material over eight recognition cycles. Eighty percent of adsorption capacity was retained after eight regeneration cycles. The specific interaction results between the amine and sulfonic acid groups and the metals that were abundant in the synthetic samples showed a comprehensive remediation study with $\text{NH}_2\text{-MIP-SO}_3\text{H}$ towards real world applications. In future research, $\text{NH}_2\text{-MIP-SO}_3\text{H}$ will be subjected to a pilot scale system approach (for example, in fixed bed columns) and other methods, such as 3D printing for questions regarding the most ideal shape for the column setting.

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