

Triazine-crosslinked polyethyleneimine for efficient adsorption and recovery of gold from wastewater

Bowen Hu^{a,1}, Ming Yang^{a,1}, He Huang^a, Zilin Song^c, Peng Tao^c, Yurui Wu^a, Kewen Tang^{a,*}, Xiaobo Chen^{b,*}, ChangAn Yang^{a,*}

^a Department of Chemistry and Chemical Engineering, Hunan Institute of Science and Technology, Yueyang, Hunan 414006, China

^b Department of Chemistry, University of Missouri – Kansas City, Kansas City, MO 64110, USA

^c Department of Chemistry, Center for Research Computing, Center for Drug Discovery, Design and Delivery (CD4), Southern Methodist University, Dallas, TX 75275, USA

ARTICLE INFO

Article history:

Received 13 April 2022

Revised 7 October 2022

Accepted 9 October 2022

Available online 15 October 2022

Keywords:

Triazine-crosslinked polyethyleneimine

Gold adsorption

Rapid adsorption

Large adsorption capacity

Fast regeneration

ABSTRACT

Recovering precious gold Au(III) ions from aqueous solution not only has a large economic incentive but also bears a significant environmental impact. One longstanding challenge is to obtain fast, effective and selective Au(III) adsorption without performance degradation. In this paper, a series of novel water-insoluble triazine-crosslinked polyethyleneimines (referred as TCPEIs, s stands for the molar ratio of amino to chlorine and s = 2, 4, 6, 8, 10) are designed and synthesized as adsorbents for Au(III) recovering from waste solutions. Excitingly, TCPEIs, TCPEI6 in particular, not only have high adsorption capacity, but also exhibit an unprecedentedly high adsorption rate. Langmuir monolayer adsorption capacities of TCPEI6 were calculated as 5462 mg/g. The adsorption efficiency of 95.6 % within 10 s with a capacity of 1073.0 mg/g and the recovering rate constant is more than 10 times greater than the best Au(III) adsorbents reported so far. Such excellent adsorption performance is mainly attributed to electrostatic interaction, complexation and the mechanical stability of TCPEIs. Furthermore, TCPEIs was regenerated within one minute to completely release the adsorbed Au(III) ions and the regenerated TCPEIs was used again for adsorb Au(III) ions, showing no apparent performance degradation, demonstrating the very attractive prospect for TCPEI6 in precious metal ion recovery.

© 2022 Elsevier B.V. All rights reserved.

Abbreviations: **GMCCR**, glycine modified crosslinked chitosan resin; **BHJC**, The agricultural residuals buckwheat hulls in the region of Jiaodong, China (BHJC); **PPF**, The persimmon residual crosslinked with formaldehyde; **LMCCR**, l-lysine modified crosslinked chitosan; **CAF**, Cellulose acetate fibers; **AER**, core-shell type anion exchange resins functionalized using ethylenediamine and 1-(2-aminoethyl) piperazine; **IECS-GLA**, Ethylenediamine N-(2-(1-imidazolyl) ethyl) glutaraldehyde-crosslinked chitosan imprinted polymer; **TCN**, thioamide-group chelating nanofiber membranes; **TSC-CC**, corn bract modified by thiosemicarbazide; **PEHA**, triazine-pentaethylene hexamine polymer; **TETA**, triazine-triethylenetetramine polymer; **EDA**, triazine-ethylenediamine polymer; **TG**, tannin gel particles; **ZIF-8**, zeolitic imidazolate framework-8; **RS-SR-NH-SF**, Thioctic acid functionalized silica coated magnetite nanoparticles; **D301-g-THIOPGMA**, D301 resin modified by thiourea; **D3-1-g-EDAPGMA**, D301 resin modified by ethylenediamine; **GH-D-P**, hybrid material silica gel modified by diethylenetriaminemethylenephosphonic acid; **AIAC**, Aliquat-336-impregnated alginate capsule; **AMPD-SNP**, The adsorbent prepared by grafting AMPD on the surface of SNP.

* Corresponding authors.

E-mail addresses: Tangkewen@sina.com (K. Tang), chenxiaobo@umkc.edu (X. Chen), Chang_anyang@hnist.edu.cn (C. Yang).

¹ These authors contributed equally to this work.

<https://doi.org/10.1016/j.molliq.2022.120586>

0167-7322/© 2022 Elsevier B.V. All rights reserved.

1. Introduction

As an important precious metal, gold is of unique physical and chemical properties and play important roles in catalysis, chemical industry, medical and other high-tech industries, as well as jewellery and electronics [1–5]. In recent years, the demand for gold has been increasing in industry and economy. However, the large-scale mining of gold leads to the continuous reduction of gold ores that are easily mined and rich in gold. Meanwhile, the frequent upgrading of electronic equipment leads to continuous reduction of gold resources and huge amount of electronic waste and environmental pollution [6–9]. However, the total reserve is constant for gold on the earth. Hence, it becomes particularly important to reduce and recycle the waste of gold in e-waste. Indeed, the gold content in e-waste is much higher than in natural resources. For example, the gold concentration in discarded mobile phones and printed circuit boards is about 200–350 g/t, much higher than 5–30 g/t in gold mines [10]. Therefore, it has attracted more and more attention to recover gold from e-waste and waste catalysts.

Nowadays, the major difficulty in gold recovery is that the conventional gold recovery methods, such as precipitation [11], ion exchange [12–13], solvent extraction [14–17], and membrane separation [18–19] involves with complex operation, high cost, and even secondary pollution, and are not energy saving and environment-friendly [20–22]. Compared to those methods, adsorption [23–26] is considered to be an effective and promising method for gold-ion adsorption, because of its low cost, easy operation, and environmentally benign. For example, Lin *et al.* reported that thiosemicarbazide-functionalized corn bract selectively adsorbed Au(III) ions from aqueous solution with a maximum adsorption amount of 1470.22 mg g⁻¹ in 24 h. The polymer retained high adsorption efficiency after three cycles (desorption time is 24 h) [27]. King Lun Yeung *et al.* constructed two types of high-efficiency gold adsorbents (named NH₂-MCM-41 and SH-MCM-41) by grafting aminopropyl and thiolpropyl groups on the surface of the mesoporous molecular sieve (MCM-41). Those two kind gold adsorbents were selective for gold adsorption through ion interaction and complexation. Gold was recovered as high purity gold chloride solutions (greater than 90 %) by elution with mineral acid for NH₂-MCM-41 and with thiosulfate for SH-MCM-41. Moreover, the regenerated adsorbent remained selective to gold and exhibited the adsorption capacity of the fresh adsorbent [28]. Tang *et al.* also reported the MOF adsorbent (ZIF-8) for Au (III) recovery with a maximum adsorption capacity of 1192 mg/g in 42 h, and the stable adsorption performance was maintained after recycle twice [29].

Polyethyleneimine (PEI), a cost-effective polymer with many primary, secondary and tertiary amine groups, has shown the attractive prospect for gold adsorption and recovery [30]. For example, Sung *et al.* reported polyethyleneimine (PEI)-coated polysulfone/*Escherichia coli* biomass composite fiber (PEI-PSBF) for Pd (II) recovery with an adsorption rate 9.28 mg/g/min, and the maximum adsorption capacity of 216.9 mg/g [30].

Nevertheless, most PEI-based adsorbents are water soluble, unstable in aqueous solutions, and have difficulty to retrieve from the solution. It has been shown that introducing PEI into the surface of biosorbent can increase the binding sites on the biomass surface, and overcome the disadvantage that PEI is a water-soluble polymer [31–35]. Dipak J. Garole *et al.* showed the gold adsorption on PEI-modified *Lagerstroemia speciosa* leaves powder (PEI-LS) was fast and reached equilibrium within 6 h and the maximum adsorption amount reached 286–313 mg/g [31]. Yeung-Sang Yun *et al.* reported the gold adsorption on alginate fiber modified with PEI (GA-PEI-Alginate). GA-PEI-Alginate reached adsorption equilibrium within about 400 min and the maximum adsorption amount of GA-PEI-Alginate reached 2300 mg/g. The loaded gold could be desorbed with thiourea/HCl mixture for five successive adsorption–desorption cycles [36].

Recently, Triazine-polyamine shows great potential in adsorbing metal chloride anions. For example, Mustafa Canet *et al.* synthesized 1,3,5-Triazine-Pentaethylenhexamine polymer (TAPEHA) for recovering Pd from chlorine containing solution. The results suggested negatively charged chloropalladium (II) can interact with TAPEHA major via ligand exchange mechanism. Hence, the TAPEHA shows a very high adsorption capacity with 517.2 mg Pd (II)/g [37]. Using TAPEHA for the adsorption of Rh(III) complexes containing chlorine ions in the aqueous solution, TAPEHA also shows excellent adsorption capacity with 327.03 mg/g [38]. Further, Mustafa Can *et al.* reported a series of triazine polyamine polymers with different amine chain lengths. These polymers exhibit excellent gold adsorption efficiency and with the increase of secondary amine content, the gold adsorption efficiency can be effectively improved [39].

Compared with other crosslinking agents, the N atoms and the rigid ring of triazine are beneficial to metal chloride anion

adsorption [37,40]. Meanwhile, the increase of amino content in the adsorbent system can also promote the adsorption of Au (III). Hence, an interesting point arises concerning what is the performance of the crossing polymers prepared by triazine and PEI containing a large amount of amino and imino in adsorbing Au (III) ions from chloride-containing solutions. With this aim, we have designed and synthesized a series of water-insoluble triazine-crosslinked polyethyleneimines (defined as TCPEIs, *s* stands for the molar ratio of amino to chlorine and *s* = 2, 4, 6, 8, 10) as adsorbent for gold adsorption and recovery. The adsorption experiment shows that TCPEIs are of excellent Au(III) adsorption performance, of which TCPEI6 is the best. Langmuir monolayer adsorption capacities of TCPEI6 were calculated as 5462 mg/g. More exciting is that TCPEIs shows ultrafast adsorption kinetics (e.g., most adsorption finish within 10 s, the recovering rate constant is 10 times greater than that of the best adsorbents), and robust adsorption/desorption reusability. In addition, the Au(III) adsorption mechanism on TCPEIs has been explored with experimental measurements and density functional theory (DFT) calculations. We hope this study can provide inspiration for future materials development for gold recovery.

2. Experimental

2.1. Materials

Polyethyleneimine (PEI, M.W. 10,000, 99 %) and 2,4,6-trichloro-1,3,5-triazine (TCT, 99 %) were purchased from Aladdin (Shanghai, China). Tetrahydrofuran (THF, ≥99 %) was provided by Beijing Chemical Co. (Beijing, China). Dimethylformamide (DMF, ≥99 %) was purchased from Sinopharm Group Chemical Reagent Co. Ltd. (Shanghai, China). AuCl₃ was obtained from Energy Chemical (Shanghai, China). THF was refluxed for 12 h prior to use. All other reagents were of analytical grade, and used without further purification, and all solutions were prepared with deionized water.

2.2. Synthetic procedures

2.2.1. Water-insoluble crosslinked polyethyleneimine

As is shown in Fig. 1, TCPEIs were prepared using the nucleophilic aromatic substitution reaction of PEI with 2,4,6-trichloro-1,3,5-triazine (TCT) at 70 °C with molar ratios from 10:1 to 2:1. This reaction produced pale-yellow precipitates with a 35–85 % yield. The detailed procedures to synthesize TCPEI6 were as follows: A 250 mL of the three-necked flask equipped with a magnetic stir bar and reflux condenser was charged with PEI (10.0 g, 1.0 mmol), DMF (20.0 mL). After the mixture was stirred to homogeneous phases at 500 rpm rate, then the solution of TCT (2.46 g, 13 mmol) in dry THF was added. After the addition was complete, the mixture was reacted at 70 °C for 36 h. Finally, the suspension was placed into ice-water bath to obtain precipitates. The solid was washed with THF and then with water several times, and freeze-dried in order to obtain water-insoluble crosslinked polyethyleneimine TCPEI6 (7.2g, 58 % yield) as a white powder.

2.2.2. The alkalization crosslinked polyethyleneimine (ATCPEI6)

A certain amount of adsorbent material TCPEI6 was dispersed in water, and a sodium hydroxide solution was added to adjust the pH to 13; the suspension was continuously stirred for 12 h, and then washed several times with deionized water and dried to obtain a product ATCPEI6.

2.2.3. Epichlorohydrin crosslinked polyethyleneimine (ECPEI6)

10 g of polyethyleneimine was added to a 500 mL three-necked flask and 20 mL of anhydrous DMF was added to the flask and

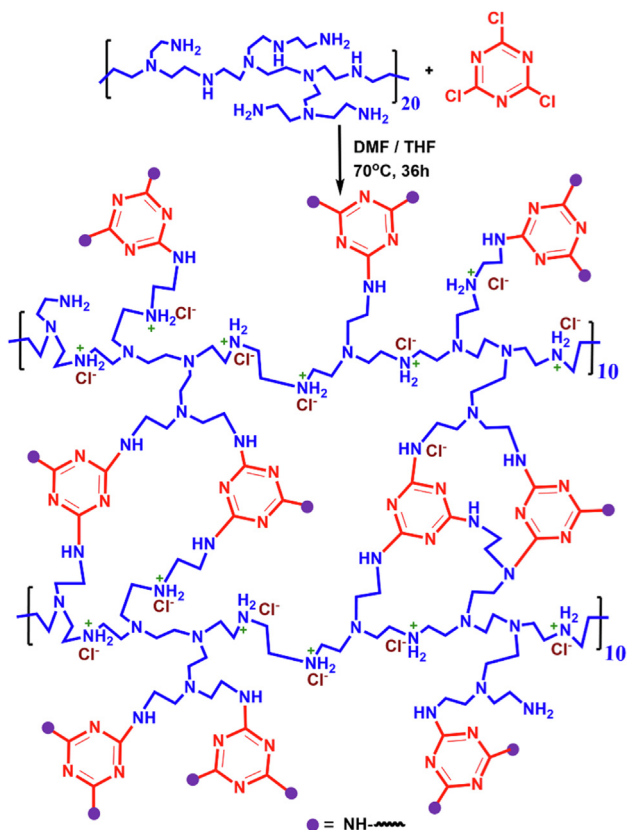


Fig. 1. Synthesis of the water-insoluble triazine-crosslinked polyethylenimine (TCPEIs) from PEI and TCT.

dissolved by stirring thoroughly at 500 rpm rate. Then 0.37 g epichlorohydrin was slowly added, and the solution was fully reacted at 70 °C for 36 h. Finally, the suspended droplets in the bottle are added to a large amount of ice water solution to obtain sediment. The solids were washed successively with water and THF to remove PEI and TCT, and then washed with water until THF was removed. Finally, a white powder porous adsorbent ECPEI6 was obtained by freeze-drying.

2.3. Instruments, measurements, and calculations

The information of instruments and related measurements along with DFT calculations are summarized in [supporting information](#).

3. Results and discussion

3.1. Structural and chemical properties

The chemical structures and compositions of TCPEIs were confirmed with elemental analysis, solid-state ^{13}C nuclear magnetic resonance (NMR) spectroscopy and Fourier transform infrared spectroscopy (FTIR). [Fig. 2](#) presented the ^{13}C NMR spectra of TCPEI6 (A), PEI (B) and trichloro-1,3,5-triazine (C). The spectra of TCPEI6 exhibited resonances associated with PEI as a broad featureless band. The peak at $\delta = 165$ ppm corresponded to the aromatic carbons of TCT, indicating that the substitution reaction between PEI and TCT was achieved and TCT was successfully inserted into PEI. The successful cross-linking of TCT between the branches of PEI was confirmed with the merge of the narrow peaks between 60 and 20 ppm of the freely moving PEI branches into one broad fea-

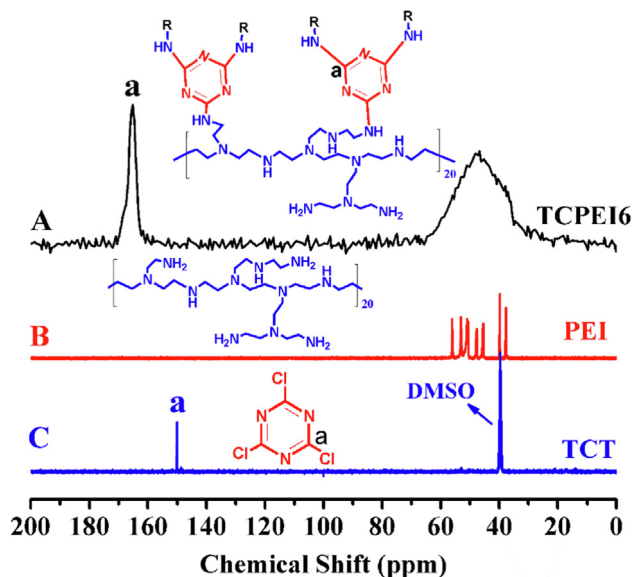


Fig. 2. (A) Solid-state ^{13}C NMR spectra of TCPEI6. ^{13}C NMR spectra of (B) PEI in D_2O and (C) TCT in $\text{DMSO-}d_6$.

tureless peak due to the formation of the rigid PEI branches fixed cross-linked by TCT in the TCPEI nanoparticles.

In [Fig. 3](#), the FTIR spectra of TCPEIs showed a peak at 1498 cm^{-1} , corresponding to thiotriazinone C–N skeletal vibrations as the IR features of TCT. The N–H stretches near 3372 cm^{-1} , C–H stretches at 2949 cm^{-1} and 2841 cm^{-1} , an intense N–H bending vibrations at 1571 cm^{-1} , and C–N stretches at 1503 cm^{-1} found in the IR spectra of TCPEIs were IR features from the PEI moiety. C–Cl stretches and C–Cl bending vibrations in the spectra of TCT, which respectively resonated at 1267 and 850 cm^{-1} , disappeared from the spectrum of TCPEIs, as expected for complete Cl substitution after the cross-linking in the TCPEIs.

3.2. Effect of crosslinking agent ratio and type of crosslinker on the Au (III) ion adsorption properties of TCPEIs

We evaluated the influence of crosslinking agent ratio on the adsorption performance of TCPEIs. The initial concentration and pH of Au(III) solutions were 560 mg/L and 7.0 , respectively and the test processes were carried out according to the following procedure. Specifically, 20 mg TCPEIs was put 40 mL HAuCl_4 solution with a concentration of 560 mg/L at 298 K to retrieve Au(III) ions. Aliquots of the suspension were taken at set intervals via syringe and filtered immediately with a $0.2\text{ }\mu\text{m}$ membrane filter and the concentrations of the Au(III) solution was determined with atomic absorption spectroscopy. [Fig. 4](#) showed the Au(III) adsorption after 5 min. Apparently, increasing the ratio of the reagents PEI/TCT from 2 to 10 (corresponding to TCPEI2, TCPEI4, TCPEI6, TCPEI8, and TCPEI10, respectively) changed the 10 s adsorption efficiency from 81.1, to 82.8, 95.6, 89.6 and 91.6 % respectively. [Fig. S1](#) showed the adsorption properties after 30 min. TCPEI6 showed the largest capacity of 1114.12 mg g^{-1} , followed by TCPEI10, TCPEI8, TCPEI4, TCPEI2. The adsorption capacity of TCPEIs depended on the number of its active adsorption sites which was largely controlled by the atomic ratio of the reagents PEI/TCT. Therefore, the results of Au(III) adsorption of polymers with different atomic ratios of the PEI/TCT suggested that TCPEI6 had the optimal composition ratio to allow the best synergy between the triazine and PEI to provide most adsorption sites for Au(III) adsorp-

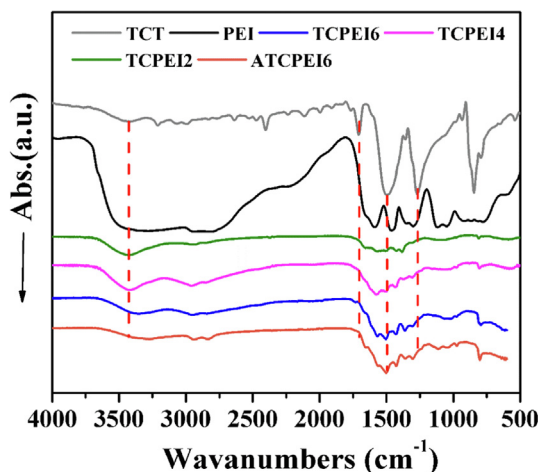


Fig. 3. FTIR spectra of PEI, TCT, TCPEI6, and ATCPEI6.

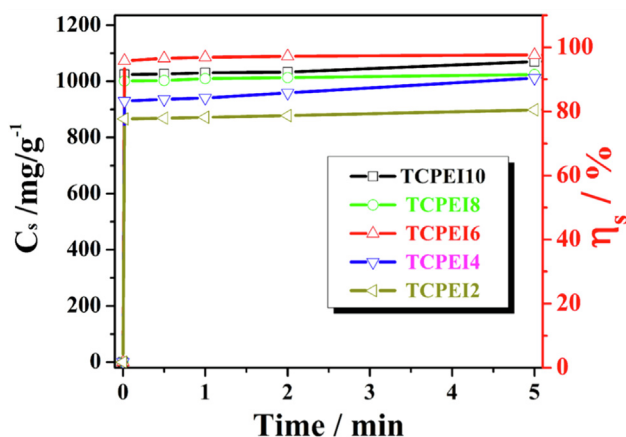


Fig. 4. 5 min stationary time-dependent Au(III) adsorption capacity (C_s) and efficiency (η_s) of aqueous Au(III) (560 mg/L) by TCPEIs ($s = 2, 4, 6, 8, 10$).

tion. As TCPEI6 exhibited the best adsorption efficiency, we focused on the study of TCPEI6 in the following studies.

According to the pervious literature [37], it was recognized that the rigid triazine ring could fill the mesopores of crosslinked polymer, increasing the absorption efficiency of adsorbent. Simultaneously, the nitrogen atom on the triazine ring could make up for the decrease of active adsorption sites caused by the introduction of crosslinker. Therefore, we believed that TCPEI6 with such excellent performance in Au(III) recovery was closely related to the crosslinking agent. In order to verify that concept, we prepared flexible crosslinking PEI polymer by using epichlorohydrin as crosslinking agent (named ECPEI6, the ratio of the reagents PEI and crosslinking agent is 6: 1). The initial concentration and pH of Au(III) solutions were also 560 mg/L and 7.0, respectively. In the 5 min adsorption performance shown in Fig. 5, the adsorption rate and maximum adsorption capacity of ECPEI were much lower than that of TCPEI6. At 10 s, the adsorption efficiency of ECPEI only showed 1.23 %, while that of TCPEI6 was as high as 95.56 %. Fig. S2 showed the 30 min adsorption performance, after 11 min, the adsorption capacity of ECPEI6 reached equilibrium, and the maximum adsorption capacity was around 932.9 mg g⁻¹, which was also much lower than 1114.12 mg g⁻¹ of TCPEI6.

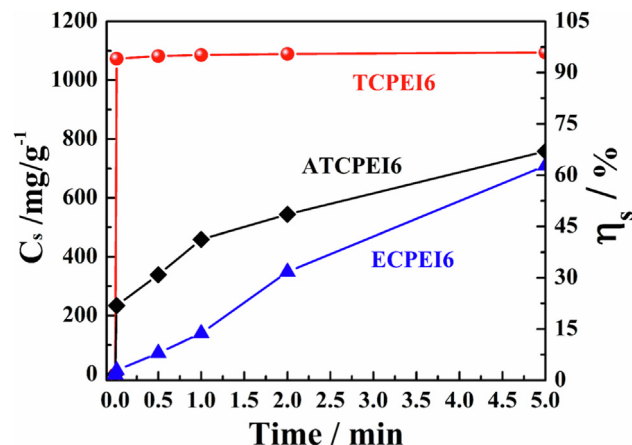


Fig. 5. 5 min stationary time-dependent Au(III) adsorption capacity (C_s) and efficiency (η_s) of aqueous Au(III) (560 mg/L) by TCPEI6, ATCPEI6 and ECPEI6.

3.3. Au(III) ion adsorption properties of TCPEI-6

As shown in Fig. 5, most (greater than 95 %) of the Au(III) adsorption was successfully finished within 10 s, demonstrating the rapid Au(III) adsorption characteristic of TCPEI6. With further increase of adsorption time, the amount of gold adsorbed by TCPEI6 increased only slightly. Finally, after 30 min of adsorption, the adsorption efficiency reached 99.23 % and the adsorption capacity was 1114.12 mg/g (seen Fig. S2). As a comparative test, we treated TCPEI6 with sodium hydroxide for 12 h to deprotonate TCPEI in forming ATCPEI6. ATCPEI6 only showed a small efficiency of 21.1 % within 10 s, and the efficiency only slowly climbed up as the adsorption time increased (seen Fig. 5). Finally, the adsorption efficiency of ATCPEI6 was 1056.86 mg/g after 30 min of adsorption (seen Fig. S2). Compared to TCPEI6, ATCPEI6 could not adsorb Au(III) by electrostatic interaction but adsorb Au(III) through hard acid-base pairing mechanism where neutral nitrogen acted as the hard base to donate electrons to the hard acid Au(III) ions featuring with unfilled 6 s and 5d orbitals. Therefore, the obvious decrease of the adsorption efficiency, especially the adsorption rate, indicated that the electrostatic interaction played a vital role than complexation in the process of TCPEI6 adsorbing Au(III), i.e., in terms of fast adsorption kinetics.

The Au(III) adsorption performance of TCPEI6 was quite encouraging because TCPEI6 retrieved Au(III) with high capacity and the adsorption rate constant of TCPEI6 was up to thousands of times faster than any gold adsorbents that have been reported [25,39–49]. Fig. 6a and b presented the comparison of Au(III) adsorption rate and capacity within 10 s and 30 min of various materials, respectively. TCPEI6 had an adsorption rate (107.3 mg g⁻¹ s⁻¹) and capacity (1073 mg g⁻¹), 14.3–5365 folds higher than other adsorbents [17,25,26,39–49]. For 30 min Au(III) recovery, TCPEI6 had an adsorption rate (0.629 mg g⁻¹ s⁻¹) and capacity (1114 mg g⁻¹), 3.83–124 folds better than other materials (Fig. 6b). This regeneration time (t_e) was 26–3000 times shorter (Fig. 7a) and correspondingly, the regeneration rate ($1/t_e$) (Fig. 7b) was 26–3000 times faster than any adsorbents reported to date [17,25,26,39–49]. These results suggested that if operated in the fast and consecutive adsorption-regeneration mode, 1.0 g TCPEI could recover up to 9.27 kg Au(III) per day, which was very attractive to recover Au(III) from wastewater.

3.4. Ion adsorption selectivity of TCPEI-6

We evaluated TCPEI6's Au(III) selectivity from both single and mixed metal ion solutions. The ions chosen were Cu(II), Cd(II), Ni

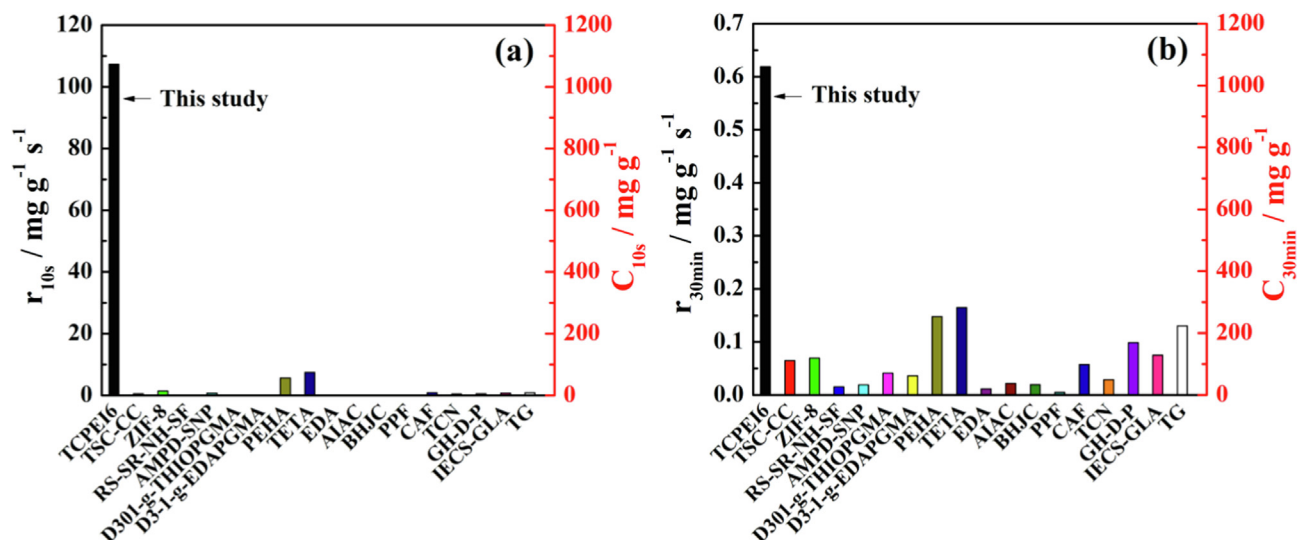


Fig. 6. Comparison of Au(III) adsorption rate and capacity within (a) 10 s and (b) 30 min of various materials. The data are obtained by dividing the adsorption amount by the adsorption time.

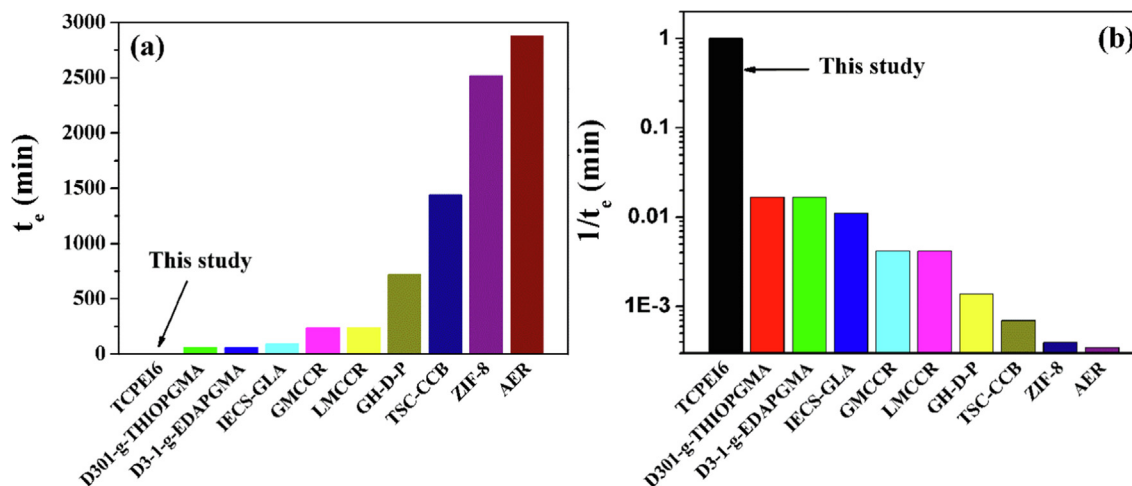


Fig. 7. Comparison of (a) elution time (t_e) and (b) elution rate ($1/t_e$) of various materials.

(II) and Pb(II) ions as they were commonly. Fig. 8a showed the results from the mixed ion solution containing same concentrations of Au(III), Cu(II), Cd(II), Ni(II) and Pb(II) ions. 97.9 % Au(III) was selectively adsorbed by TCPEI6, in comparison to 1.79 % Cd (II), 3.06 % Cu(II), 1.52 % Ni(II) and 1.97 % Pb(II). TCPEI6 showed a very high selectivity of 32.0–64.4 in recovering Au(III) over other metal ions from the mixed ion solution, likely due to the favored affinity between nitrogen sites and Au(III) over other coexisting ions. The experiments using single ion solutions also confirmed the results (Fig. 8b), with a selectivity up to 99.1 of Au(III) ions over other ions. Compared with other metal elements, only Au can form $AuCl_4^-$, which is selectively captured by positively charged TCPEIs through electrostatic interaction.

3.5. Regeneration and desorption kinetics

It is important for adsorbent to have good reusability and a short regeneration time, for practical use with low operational cost. We examined the regeneration and reusability properties of TCPEI6. A HCl solution containing thiourea is used to regenerate TCPEI6 and at the same time obtain a concentrated Au(III) solution.

Fig. 9a showed that TCPEI6 was regenerated within one minute to completely release the adsorbed Au(III) ions. The regenerated TCPEI6 was used again for adsorb Au(III) ions, showing no apparent performance degradation, as demonstrated in the five consecutive adsorption experiments shown in Fig. 9b. As shown in Fig. 9c, the desorption efficiency (η_d) for TCPEI6 was nearly 100 % within 1 min.

3.6. Effect of solution pH on the Au(III) adsorption properties of TCPEI6

As we expect that the electrostatic interactions between the positively charged protonated TCPEI6 and the negatively charged $AuCl_4^-$ complex was the key to the rapid adsorption of Au(III) by TCPEI6, and the solution pH would affect the protonation of TCPEI6, therefore, the Au(III) adsorption performance. Hence, we studied the effect of solution pH on the efficiency of TCPEI6 adsorbing Au(III) in detail, to determine the suitable pH for TCPEI6.

As shown in Fig. 10a, the zero-point charge (pH_{zpc}) of TCPEI6 was 11.6. This suggested that below pH 11.6, TCPEI6 was positively charged due to its numerous protonated imine/amine groups, to adsorb the negatively charged $AuCl_4^-$ complex where Au(III) ions

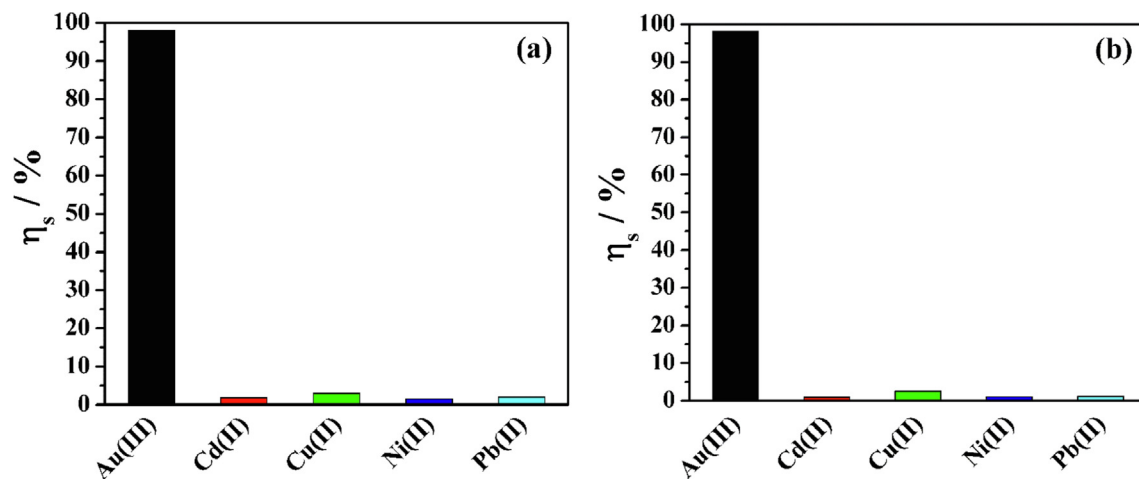


Fig. 8. Adsorption of TCPEI6 for different metal ions (a) from the mixed ion solution and (b) from the single ion solutions. (Conditions: $m = 10$ mg, $C = 500$ mg·L⁻¹, $V = 20$ mL, $T = 298$ K, $pH = 2$, Contact time = 1 h).

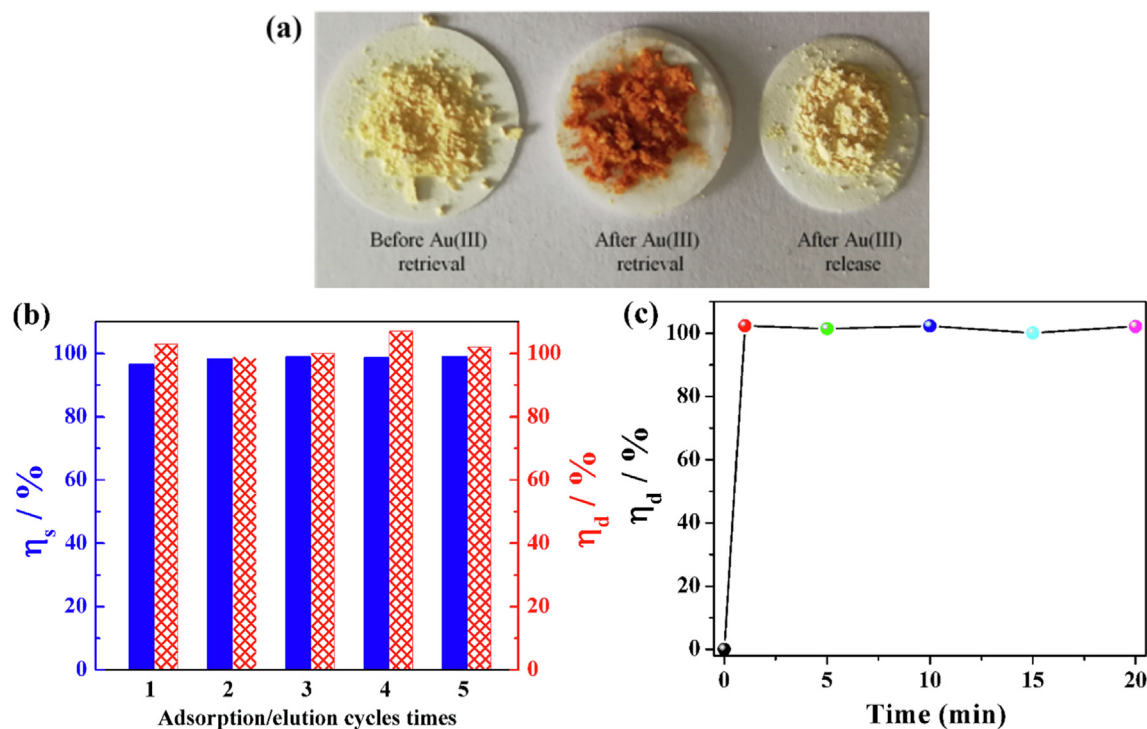


Fig. 9. (a) Photographs of TCPEI6 before Au(III) adsorption, after Au(III) adsorption and after Au(III) release and TCPEI6 regeneration. (b) adsorption efficiency (η_s) and desorption efficiency (η_d) of Au(III) by TCPEI6 in consecutive regeneration cycles. (c) Time-dependent desorption efficiency (η_d) of TCPEI6 (Conditions: $m = 5.0$ mg, $C = 400$ mg·L⁻¹, $V = 10$ mL, $T = 298$ K, Desorption agent: 10 mL 5 % solution of thiourea in 3.0 M HCl).

existed in aqueous solution from pH 1.0 to 12.0 [50]. Therefore, the electrostatic interaction allowed fast Au(III) ion adsorption with a large capacity provided by the numerous protonated imine/amine groups within TCPEI. This also suggested that TCPEI6 would have outstanding performance over a broad pH range.

So we further measured the absorption of TCPEI6 to Au(III) under various pH values and found that most of the Au(III) adsorption was achieved within 2 min across all the pH values. The observed adsorption efficiency was 98.6–97.9 % when the pH was 2.0–6.0, and slightly decreased to 91.6 % at pH = 9.0 and then 73.7 % at pH = 11.0 (Fig. 10a). As shown in Fig. 10b, when the adsorption time increased to 30 min, the adsorption efficiency was robust (about 97.0 %) in a wider pH range of 2.0–9.0, and

dropped to 92.1 and 82.3 % at pH = 10.0 and 11.0, respectively. Therefore, if TCPEI6 is used for fast or flow operation, the optimal pH range was 2.0–6.0; for stationary operation, the optimal pH range was 2.0–9.0. The drop of the ion adsorption near pH 10.0 further verified the importance of the quaternary ammonium salt for the fast recovery of Au(III) ions and validated our concept in creating TCPEI6 for efficient Au(III) recovery.

3.7. Isotherm and kinetic models for the Au(III) adsorption properties of TCPEI6

The adsorption kinetics of Au(III) on TCPEI6 was also studied with the concentration-dependent isotherm adsorption curve.

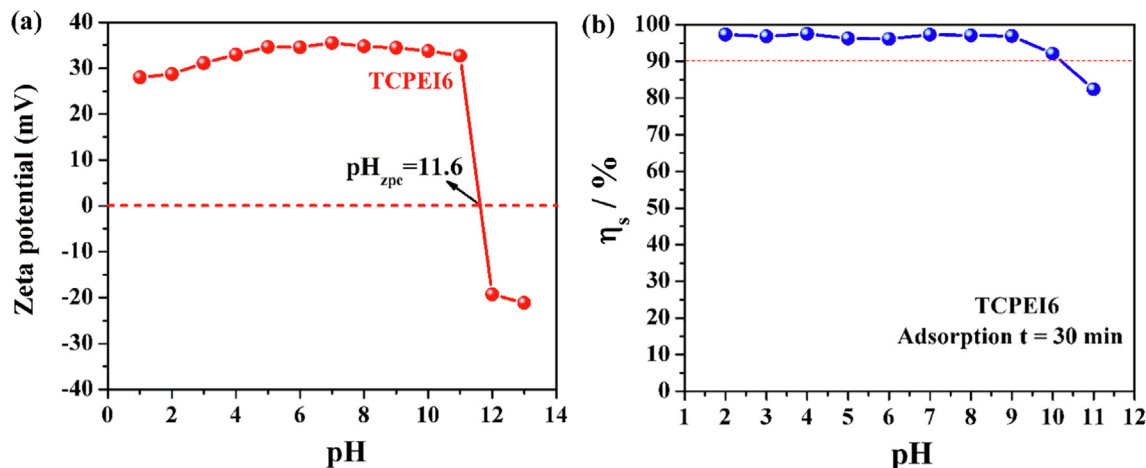


Fig. 10. (a) Effect of initial pH for zeta potential of TCPEI6 and (b) effect of solution pH on the adsorption efficiency of TCPEI6.

Fig. 11 showed that the Au(III) adsorption capacity increased monotonically with the initial Au(III) concentration. A large equilibrium Au(III) adsorption capacity of 5386.5 mg g^{-1} was observed when the initial Au(III) concentration increased to 2175.6 mg L^{-1} .

The classical adsorption models, namely Langmuir and Freundlich equations, were evaluated to describe the experimental adsorption results of Au(III) on TCPEI6. The linearized forms of Langmuir isotherm model (Eq. (1)) and Freundlich isotherm model (Eq. (2)) were expressed with the following equations:

$$C_e/q_e = 1/Q_{\max}K_L + C_e/Q_{\max} \quad (1)$$

$$\log q_e = \log K_F + 1/n \log C_e \quad (2)$$

In both models, q_e and C_e are the amount of Au(III) adsorbed (mg/g) and the adsorbate concentration in the aqueous phase (mg/L), both at equilibrium. $Q_{\max}$ is the maximum monolayer adsorption capacity of TCPEI6 for Au(III) (mg/g), K_L is the Langmuir isotherm constant related to the affinity of the binding sites and energy of adsorption (L/mg), K_F and $1/n$ represent Freundlich isotherm constants relating to adsorption capacity and adsorption intensity, respectively. By plotting a linear relationship of k versus contact time t (min).

Fig. 12a and b presented the fitting plots of Langmuir isotherm model and Freundlich isotherm model of Au(III) adsorption by

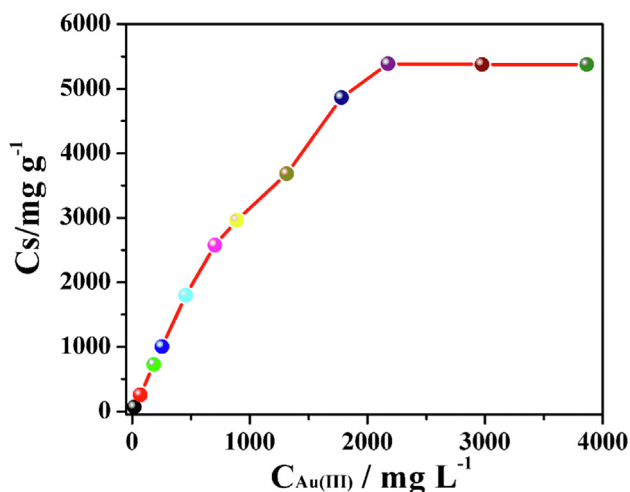


Fig. 11. The effect of initial Au(III) concentration on the adsorption capacity (C_s) of TCPEI6.

TCPEI6, respectively. The Langmuir isotherm fit the Au(III) adsorption isotherm well with the correlation coefficient (R^2) = 0.9845, better than that of Freundlich isotherm model with the R^2 = 0.8920. Hence, the adsorption as a monolayer on a surface was likely the main mechanism.

In order to further verify whether the adsorption process was dominated by physical or chemical adsorption mechanisms, two classical kinetic models were employed: pseudo-first-order (Eq.3) and pseudo-second-order (Eq.4) models as shown in the following:

$$\log(q_e - q_t) = \log q_e - k_1 t/2.303 \quad (3)$$

$$t/q_t = 1/k_2 q_e^2 + t/q_e \quad (4)$$

where k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) was the pseudo-first order and pseudo-second-order rate constant, respectively. q_e and q_t (mg/g) represented the adsorption capacity at equilibrium and time t (min).

Fig. 13 and Table 1 showed the fitting plots of pseudo-first-order and pseudo-second-order models of Au(III) adsorption of TCPEI6 and related parameters. Pseudo-second-order model seemed more suitable for TCPEI6 due to the larger correlation coefficient (R^2 = 0.99998 than that (R^2 = 0.94444) of pseudo-first-order model. This indicated that Au(III) adsorption on TCPEI6 was more likely a chemisorption process, which might involve valence forces by chelation and ion exchange. The rate constant k_2 value of $0.0201 \text{ mg g}^{-1} \text{ min}^{-1}$, at least 13 times greater than other adsorbents including MOFs [17,25,26,29,39–49]. The superior k_2 indicated that nearly all binding sites were readily accessible, likely from the creation of many mesopores and micropores by the crosslinking of TCT between the PEI branches to allow better access of the Au(III) solution.

3.8. Au(III) adsorption mechanism on TCPEI

The conceived mechanism of Au(III) adsorption by TCPEI6 was largely supported by the chemical and structural changes of TCPEI6 before and after Au(III) adsorption, and after regeneration, as revealed by the results obtained from measurements using X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), FTIR, and scanning electron microscopy (SEM). As shown in the XRD patterns in Fig. 14, TCPEI6 had one broad and weak peak near 2θ = 24.1° from the low crystallinity polymeric characteristics. After Au(III) adsorption, it had several extra, narrow and sharp peaks near 38.1 , 44.4 , 64.5 , 77.6 and 81.7° matching well with metallic gold [43–44]. This indicated that partial Au(III) was reduced into metallic

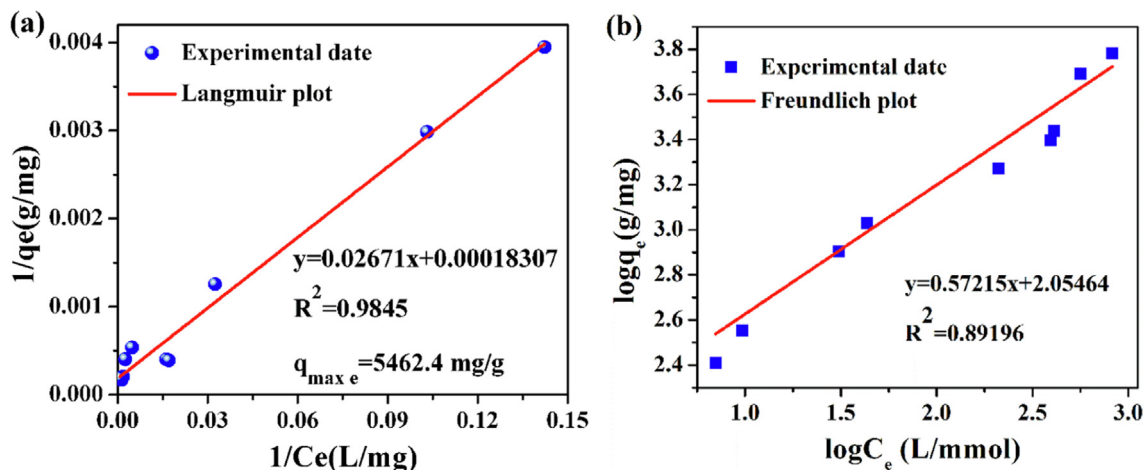


Fig. 12. (a) Langmuir and (b) Freundlich isotherm model fitting curves of Au(III) adsorption onto the TCPEI6.

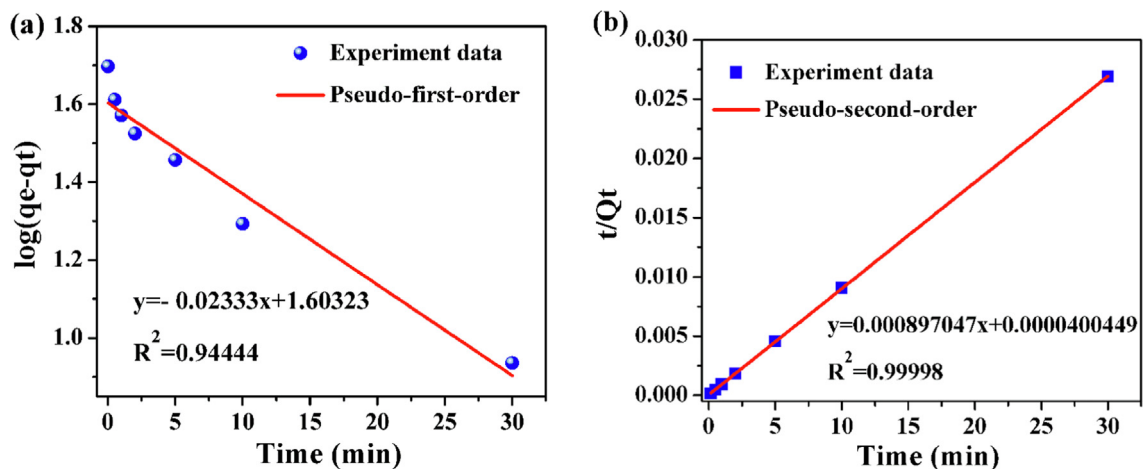


Fig. 13. (a) pseudo-first order and (b) pseudo-second order model fitting curves of Au(III) adsorption onto the TCPEI6.

Table 1

Fitting parameters of Au(III) adsorption kinetics.

Sorbent	Measured	Quasi-first-order kinetic model			Quasi-second-order kinetic model		
	q_e (mg/g)	q_e (mg/g)	k_1 (min ⁻¹)	R^2	q_e (mg/g)	k_2 (g mg ⁻¹ min ⁻¹)	R^2
TCPEI10	1091	87.99	0.0269	0.775	1268.8	0.0071	0.99996
TCPEI8	1069	125.66	0.0199	0.9713	1248.6	0.0042	0.99989
TCPEI6	1114	40.11	0.0537	0.9444	1114.7	0.0201	0.99998
TCPEI4	1107	168.07	0.0856	0.9456	1112.2	0.00384	0.99972
TCPEI2	1029	203.97	0.0568	0.9697	1033.9	0.00311	0.99921

form. After Au release for TCPEI6 regeneration, it only had one broad and weak peak near 24.1°, similar to the pristine TCPEI6. This suggested the complete regeneration and robust structural stability of TCPEI6 for Au(III) adsorption.

As shown in Fig. 15, TCPEI6 had an average particle size around 200 nm forming some large aggregations with apparent pores. After Au(III) adsorption, its porous structure was covered with adsorbed gold particles (Fig. 15b and Fig. S3–S5). After Au(III) release, TCPEI6 was fully regenerated with its original morphologies (Fig. 15c).

The surface area of TCPEI changed from 18.3, to 44.1, 9.76, 7.47 and 1.17 m²/g (Fig. S6) while the pore size distribution did not

change much (Fig. S7), from sample TCPEI2 to TCPEI10 (with the atomic ratio of amino to chlorine from 2 to 10). Apparently, the Au(III) adsorption properties of TCPEIs had no straightforward relationship with its surface area or pore size distribution (Fig. S8 and Fig. S9). This indicated that the adsorption did not depend on the surface area and pore size distribution, benefiting from the chemical adsorption characteristics and the easy access from the Au(III) to the binding sites in TCPEIs.

The Au(III) adsorption on TCPEI were further analyzed with XPS spectra of TCPEI before and after Au(III) adsorption (Fig. 16a). As shown in Fig. 16b, after adsorbed on TCPEI6, gold existed as Au⁰ (4f_{7/2} at 86.32 eV and 4f_{5/2} at 89.8 eV), Au⁺ (4f_{7/2} at 83.5 eV and

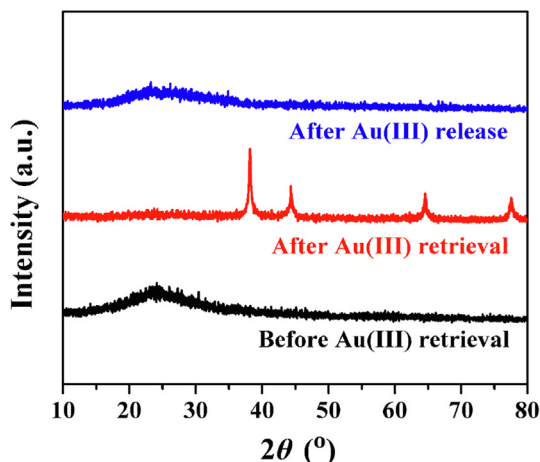


Fig. 14. 1D WAXD patterns of TCPEI6.

$4f_{5/2}$ at 86.9 eV) and Au^{3+} ($4f_{7/2}$ at 84.6 eV and $4f_{5/2}$ at 87.7 eV) [43,51], with the corresponding atomic ratio of 1: 3.6: 2.59. The appearance of gold with lower oxidation states indicated that chemical reduction occurred during the adsorption.

Nitrogen atoms in TCPEI6 appeared in the forms of $C=N$ (397.4 eV), $-NH/-NH_2$ (399.1 eV), $-N$ (398.3 eV) and $-NH_2^+$ (399.5 eV) with the corresponding atomic ratio of 1: 0.76: 0.84: 1.03, based on the N1s spectrum in Fig. 16c. After Au(III) adsorption, their peaks shifted to higher energies: 397.7, 399.2, 398.7, and 400.1 eV, respectively, indicating of oxidation by the adsorbed gold ions. Additionally, the ratio changed to 1:0.54: 0.36: 0.69 and (Fig. 16d), showing a lower percentage of the $-NH_2^+$, $-N$ and $-NH/-NH_2$. This is another indicator for the oxidation of the nitrogen site. This is consistent with the chemical adsorption from the chelation with gold ions [43–49].

After Au(III) release from TCPEI6 in the regeneration process, the nitrogen peak positions and ratio shifted back (Fig. 16e), as a results of the reduction of the imine/amine groups, since the $C=N$ group in the triazine ring could not be oxidized or reduced by transition metals but only to interact with Au(III) ions by physical adsorption [49].

To further help understanding the Au(III) adsorption properties of the TCPEIs, we performed quantum chemical calculations using DFT to identify the pattern of Au adsorption in TCPEI materials (see supporting information for computational details). To simplify the calculation process, we replaced the entire PEI polymer with *n*-methyl ethylenediamine (NMEA), the repeating structural of PEI, to complete the modeling. The energetics of Au adsorption was systematically assessed with 22 adsorption complex models (Figs. S10–S12 and Table S3). The adsorption of $AuCl_4$ by neutral model molecules, with NMEA as model for PEI and melamine as model for triazine linker, was generally exothermic (Fig. 17(a)–(d)). Adsorption of neutral $AuCl_3$ on NMEA without the presence of melamine were energetically favorable (Fig. 17(e)–(f)). The adsorption of $AuCl_3$ on melamine with different nitrogen atoms (Fig. 17(g)–(h)) were endothermic, indicating that the triazine groups may not contribute directly to the adsorption function as adsorption site at least for $AuCl_3$ groups. While the combination of adsorption of $AuCl_{x=2,3}$ on NMEA and with a neutral melamine group was remarkably exothermic (Fig. 17(i)–(j)), suggesting the unique synergy of triazine groups and NMEA in TCPEI on the adsorption. Notably, the adsorption of $AuCl_4$ with the presence of protonated NMEA and melamine groups were the most exothermic among all the model systems presented (Fig. 17(k)–(l)). This indicated that adsorption was feasible for TCPEI to adsorb under acidic condition, which was commonly applied in the leaching process with concentrated HCl in the recovery of e-waste, for example. In addition, the vibrational spectra (Figs. S13–S38) calculated by DFT were consistent with experimental measurements (Fig. S39). Therefore, a fast and large adsorption is enabled with TCPEI for gold recovery.

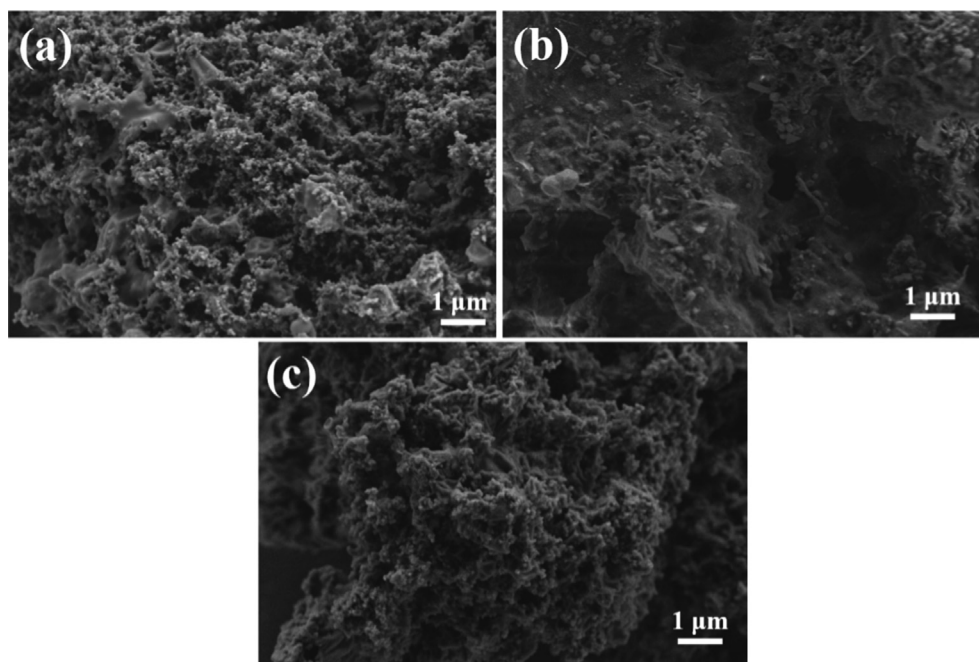


Fig. 15. SEM images of TCPEI before (a) and after (b) Au(III) adsorption, and after Au(III) release (c).

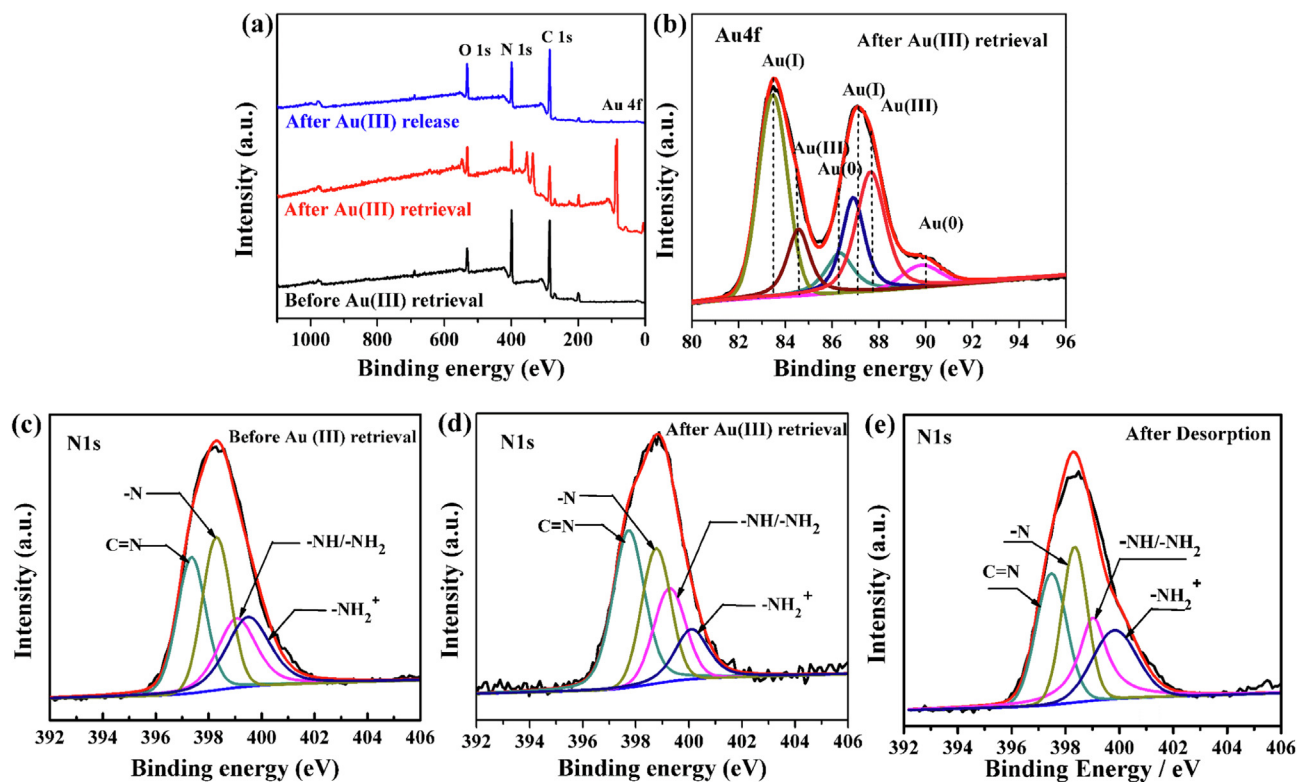


Fig. 16. (a)XPS spectra of TCPEI before and after Au(III) adsorption, and after Au(III) release. (b)Au 4f core-level XPS spectrum of TCPEI6 after Au(III) adsorption. (c)N1s core-level XPS spectrum of TCPEI6 before Au(III) adsorption. (d)N1s core-level XPS spectrum of TCPEI6 after Au(III) adsorption. (e)N1s core-level XPS spectrum of TCPEI6 after Au(III) release.

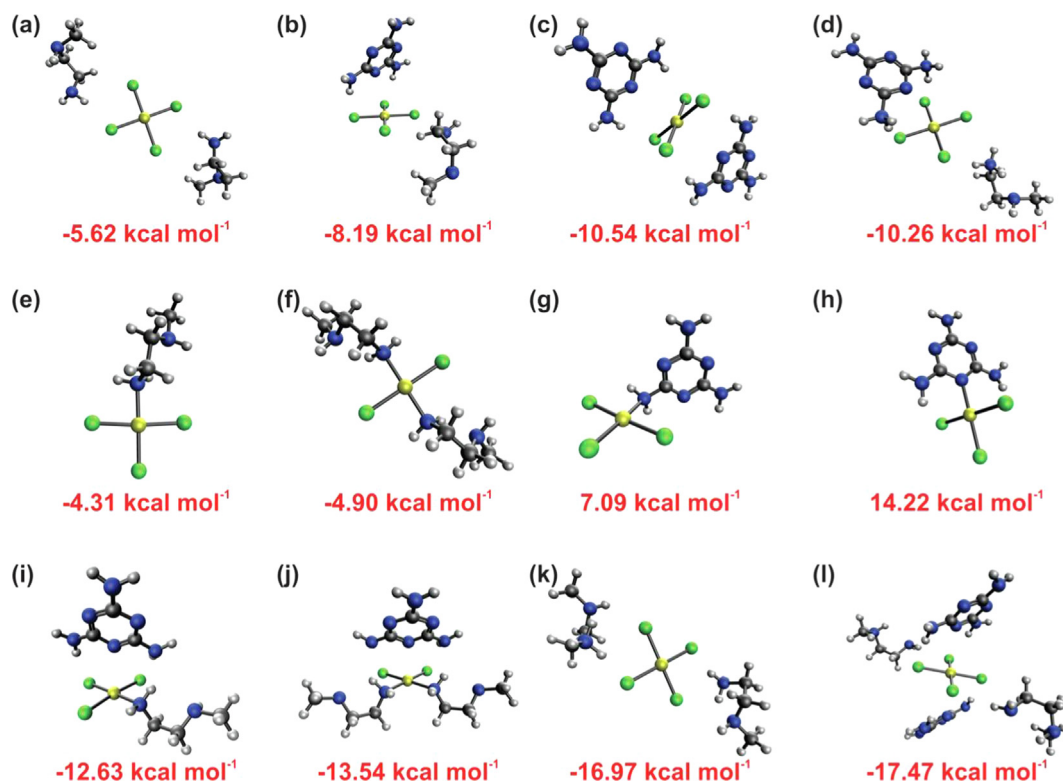


Fig. 17. Theoretical prediction on the Au(III) adsorption mechanism. AuCl₄ adsorbed with (a) neutral *n*-methyl ethylenediamine (NMEA) as model for PEI unit, (b) a neutral NMEA and a neutral melamine; (c) two neutral melamines and (d) a protonated NMEA and a protonated melamine; (e) AuCl₃ adsorbed with one neutral NMEA, (f) two neutral NMEAs, (g) amine group of a neutral melamine; (h) with nitrogen on the aromatic ring of a neutral melamine and with a neutral NMEA and a neutral melamine; (j) AuCl₂ adsorbed with two neutral NMEAs and a neutral melamine; (k) AuCl₄ physisorbed with two protonated NMEA; (M) AuCl₄ adsorbed with two neutral NMEA and melamine. The complexation energies are colored in red. Carbon atoms are in gray; hydrogen atoms are in white; nitrogen atoms are in blue; chlorine atoms are in green, and gold atoms are in yellow.

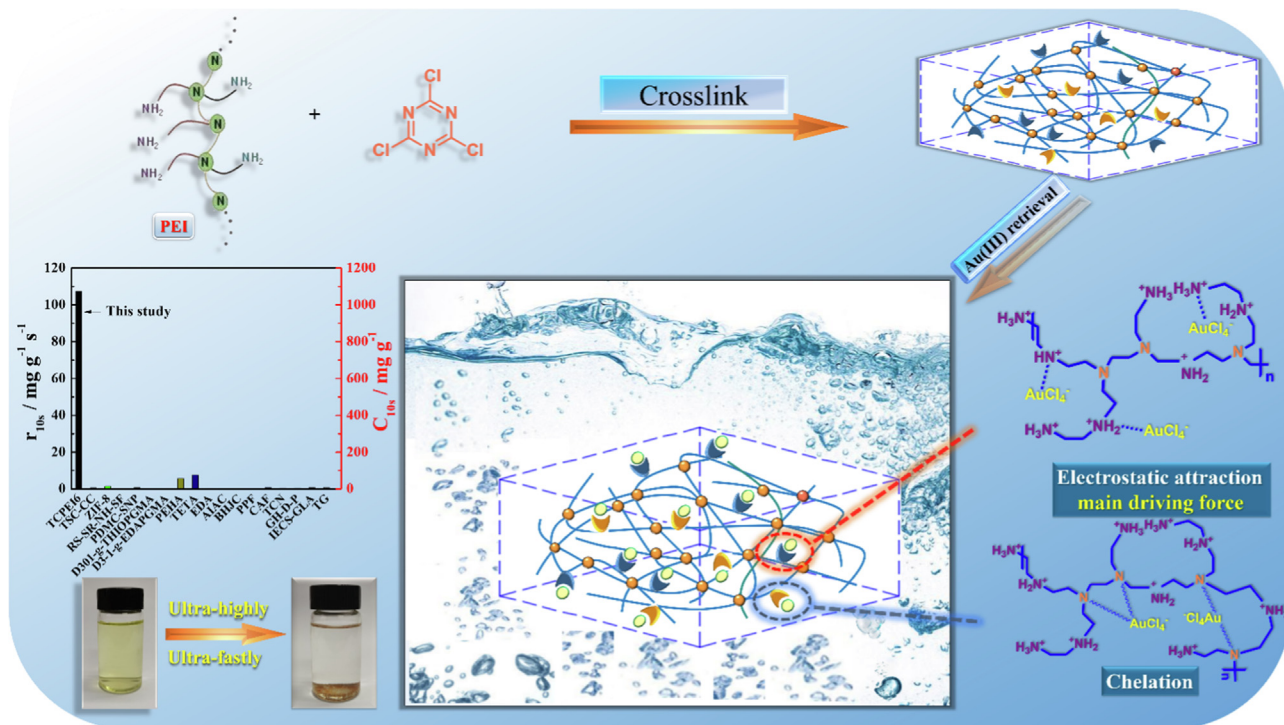


Fig. 18. Illustration of Au(III) adsorption process by TCPEIs.

Therefore, based on the above analysis, the Au(III) adsorption by TCPEIs can be summarized as shown in Fig. 18.

4. Conclusion

In summary, we have designed and prepared a series of novel water-insoluble triazine-crosslinked polyethyleneimines (TCPEIs) as adsorbent for Au(III) recovery from waste solution. Best performance can be obtained upon optimal composition of TCPEI with a good synergy between the triazine and PEI to provide most adsorption sites for Au(III) adsorption. Exciting, TCPEIs can not only have high adsorption capacity, but also maintain an unprecedented adsorption rate. The adsorption efficiency up to 95.6 % can be reached within 10 s with a capacity of 1073.0 mg/g, displaying a recovering rate constant up to 10 times faster than any other Au(III) adsorbents reported. Furthermore, robust adsorption is demonstrated over consecutive operations. The successful crosslinking of PEI branches by TCT allow the robust mechanical and adsorption stability to allow the fast, robust and selective adsorption of Au(III) ions, overcoming the shortcomings of other competing adsorbents. The impressive adsorption is enabled from both complexation and electrostatic adsorption for Au(III) ions recovery by TCPEIs. Therefore, this work may not only provide some exciting results, but also inspire some new concept and ideas for adsorbent development towards practical Au(III) recovery applications, eventually adopted by industries.

CRediT authorship contribution statement

Bowen Hu: Conceptualization, Data curation, Writing – original draft. **Ming Yang:** Conceptualization, Methodology, Writing – review & editing. **He Huang:** Investigation, Visualization. **Zilin Song:** Formal analysis. **Peng Tao:** Formal analysis. **Yurui Wu:** Validation. **ChangAn Yang:** Conceptualization, Supervision, Writing – review & editing, Funding acquisition. **Kewen Tang:**

Writing – review & editing, Resources. **Xiaobo Chen:** Methodology, Writing – review & editing, Funding acquisition.

Data availability

The data that has been used is confidential.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work was supported by National Natural Science Foundation of China (No. 52073088, U20A20268), and Scientific Research Fund of Hunan Provincial Education Department (No. 18A319, 19B235). X. C. acknowledges the support from the School of Biological and Chemical Sciences, University of Missouri - Kansas City. P. T. acknowledges the support from the U.S. National Science Foundation (No. 1753167). Computational time was provided by the Southern Methodist University's Center for Research Computing. The authors thank Professor Zhonghua Peng from UMKC for contributions to the revision of this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2022.120586>.

References

- [1] N.V. Nguyen, J.C. Lee, S.K. Kim, M.K. Jha, K.S. Chung, J. Jeong, Adsorption of gold (III) from waste rinse water of semiconductor manufacturing industries using Amberlite XAD-7HP resin, *Gold Bull.* 43 (2010) 200–208.
- [2] D. Ventura-Espinosa, S. Sabater, J.A. Mata, Enhancement of gold catalytic activity and stability by immobilization on the surface of graphene, *J. Catal.* 352 (2017) 498–504.
- [3] S. Vial, R.L. Reis, J.M. Oliveira, Recent advances using gold nanoparticles as a promising multimodal tool for tissue engineering and regenerative medicine, *Curr. Opin. Solid State Mater. Sci.* 21 (2017) 92–112.
- [4] O.A. Kirichenko, N.A. Davshan, E.A. Redina, G.I. Kapustin, I.V. Mishin, O.P. Tkachenko, A.V. Kuchero, L.M. Kustov, Gold nanoparticles in environmental catalysis: Influence of the Fe-modified alumina supports on the catalytic behavior of supported gold nanoparticles in CO oxidation in the presence of ammonia, *Chem. Eng. J.* 292 (2016) 62–71.
- [5] E.B. Nursanto, H.S. Jeon, C. Kim, M.S. Jee, J.H. Koh, Y.J. Hwang, B.K. Min, Gold catalyst reactivity for CO₂ electro-reduction: From nano particle to layer, *Catal. Today* 260 (2016) 107–111.
- [6] M. Zhu, W. Zhang, Y. Li, L. Gai, J. Zhou, W. Ma, Multishell structured magnetic nanocomposites carrying a copolymer of pyrrole–thiophene for highly selective Au(III) recovery, *J. Mater. Chem. A* 4 (2016) 19060–19069.
- [7] J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, Metal-organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions, *Chem. Soc. Rev.* 47 (2018) 2322–2356.
- [8] Z. He, L. He, J. Yang, Q. Lü, Removal and recovery of Au(III) from aqueous solution using a low-cost lignin-based biosorbent, *Ind. Eng. Chem. Res.* 52 (2013) 4103–4108.
- [9] I. Kim, H.Y. Son, M.Y. Yang, Y.S. Nam, Bioinspired design of an immobilization interface for highly stable, recyclable nanosized catalysts, *ACS Appl. Mater. Interfaces* 7 (2015) 14415–14422.
- [10] M. Gurung, B.B. Adhikari, H. Kawakita, K. Ohto, K. Inoue, S. Alam, Selective recovery of precious metals from acidic leach liquor of circuit boards of spent mobile phones using chemically modified persimmon tannin gel, *Ind. Eng. Chem. Res.* 51 (2012) 11901–11913.
- [11] A. Behnamfar, M.M. Salarirad, F. Veglio, Process development for recovery of copper and precious metals from waste printed circuit boards with emphasis on palladium and gold leaching and precipitation, *Waste. Manag.* 33 (2013) 2354–2363.
- [12] H. Murakami, S. Nishihama, K. Yoshizuka, Separation and recovery of gold from waste LED using ion exchange method, *Hydrometallurgy* 157 (2015) 194–198.
- [13] P. Cyganowski, K. Garbera, A. Leńiewicz, J. Wolska, P. Pohl, D. Jermakowicz-Bartkowiak, The recovery of gold from the aqua regia leachate of electronic parts using a core-shell type anion exchange resin, *J. Saudi Chem. Soc.* 21 (2017) 741–750.
- [14] A.M. Petrova, A.E. Nikolaev, A.G. Kasikov, J. Russian, Extraction of gold(III) from hydrochloric acid solutions with high-molecular aliphatic alcohols, *Appl. Chem.* 87 (2014) 234–240.
- [15] Y. Sasaki, K. Morita, M. Saeki, S. Hisamatsu, K. Yoshizuka, Precious metal extraction by N, N, N', N'-tetraoctyl-thiodiglycolamide and its comparison with N, N, N', N'-tetraoctyl-diglycolamide and methylimino-N, N'-dioctylacetamide, *Hydrometallurgy* 169 (2017) 576–584.
- [16] H. Vojoudi, A. Badieli, A. Banaei, S. Bahar, S. Karimi, G. MohammadiZiarani, M.R. Ganjali, Extraction of gold, palladium and silver ions using organically modified silica-coated magnetic nanoparticles and silica gel as a sorbent, *Microchim. Acta* 184 (2017) 3859–3866.
- [17] A. M.E.H. X.Y. Mbianda, A.F. Mulaba-Bafubandi, L. Marjanovic, Selective extraction of gold(III) from metal chloride mixtures using ethylenediamine N-(2-(1-imidazolyl)ethyl) chitosan ion-imprinted polymer, *Hydrometallurgy* 140 (2013) 1–13.
- [18] L.F. Villalobos, T. Yapici, K.V. Peinemann, Poly-thiosemicarbazide membrane for gold recovery, *Sep. Purif. Technol.* 136 (2014) 94–104.
- [19] G. Argiropoulos, R.W. Cattrall, I.C. Hamilton, S.D. Kolev, R. Paimin, The study of a membrane for extracting gold(III) from hydrochloric acid solutions, *J. Membr. Sci.* 138 (1998) 279–285.
- [20] S. Zhou, X. Mo, W. Zhu, W. Xu, K. Tang, Y. Lei, Selective adsorption of Au(III) with ultra-fast kinetics by a new metal-organic polymer, *J. Mol. Liq.* 319 (2020) 114125.
- [21] Z. Ren, X. Jiang, L. Liu, C. Yin, S. Wang, X. Yang, Modification of high-sulfur polymer using a mixture thioether and its application as advanced adsorbents for Au(III) from wastewater, *J. Mol. Liq.* 328 (2021) 115437.
- [22] S. Mincke, T.G. Asere, I. Verheye, K. Folens, F.V. Bussche, L. Lapeire, K. Verbeken, P. Van Der Voort, D.A. Tessema, F. Fufa, G.D. Laing, C.V. Stevens, Functionalized chitosan adsorbents allow recovery of palladium and platinum from acidic aqueous solutions, *Green, Chem* 21 (2019) 2295–2306.
- [23] S.O. Yong, J. Choong, Selective adsorption of the gold–cyanide complex from waste rinse water using Dowex 21K XLT resin, *J. Ind. Eng. Chem.* 20 (2014) 1308–1312.
- [24] B. Pangeni, H. Paudyal, M. Abe, K. Inoue, H. Kawakita, K. Ohto, B.B. Adhikari, S. Alam, Selective recovery of gold using some cross-linked polysaccharide gels, *Green Chem.* 14 (2012) 1917–1927.
- [25] K. Deng, P. Yin, X. Liu, Q. Tang, R. Qu, Modeling, analysis and optimization of adsorption parameters of Au(III) using low-cost agricultural residuals buckwheat hulls, *J. Ind. Eng. Chem.* 20 (2014) 2428–2438.
- [26] J. Yang, F. Kubota, Y. Baba, N. Kamiya, M. Goto, One step effective separation of platinum and palladium in an acidic chloride solution by using undiluted ionic liquids, *Carbohydr. Polym.* 111 (2014) 768–774.
- [27] G. Lin, S. Wang, L. Zhang, T. Hu, J. Peng, S. Cheng, L. Fu, Synthesis and evaluation of thiosemicarbazide functionalized corn bract for selective and efficient adsorption of Au(III) from aqueous solutions, *J. Mol. Liq.* 258 (2018) 235–243.
- [28] K.F. Lam, C.M. Fong, K.L. Yeung, G. McKay, Selective adsorption of gold from complex mixtures using mesoporous adsorbents, *Chem. Eng. J.* 145 (2008) 185–195.
- [29] C. Hu, W. Xu, X. Mo, H. Li, S. Zhou, P. Zhang, K. Tang, Efficient adsorption toward precious metal from aqueous solution by zeolitic imidazolate framework-8, *Adsorption* 24 (2018) 733–744.
- [30] C.W. Cho, S.B. Kang, S. Kim, Y.S. Yun, S.W. Won, Reusable polyethylenimine-coated polysulfone/bacterial biomass composite fiber biosorbent for recovery of Pd(II) from acidic solutions, *Chem. Eng. J.* 302 (2016) 545–551.
- [31] B.C. Choudhary, D. Paul, A.U. Borse, D.J. Garole, Surface functionalized biomass for adsorption and recovery of gold from electronic scrap and refinery wastewater, *Sep. Purif. Technol.* 195 (2018) 260–270.
- [32] F. Zhao, E. Repo, Y. Song, D. Yin, S.B. Hammouda, L. Chen, S. Kalliola, J. Tang, K.C. Tam, M. Sillanpää, Polyethylenimine-cross-linked cellulose nanocrystals for highly efficient recovery of rare earth elements from water and a mechanism study, *Green. Chem.* 19 (2017) 4816–4828.
- [33] A. Yasin, Y. Chen, Y. Liu, L. Zhang, X. Zan, Y. Zhang, Hyperbranched multiple polythioamides made from elemental sulfur for mercury adsorption, *Polym. Chem.* 11 (2020) 810–819.
- [34] Z. Li, R. Chen, Y. Wang, L. Zhu, W. Luo, Z. Zhang, N. Hadjichristidis, Solvent and catalyst-free modification of hyperbranched polyethylenimines by ring-opening-addition or ring-opening-polymerization of N-sulfonyl aziridines, *Polym. Chem.* 12 (2021) 1787–1796.
- [35] S.W. Won, J. Park, J. Mao, Y.S. Yun, Utilization of PEI-modified Corynebacterium glutamicum biomass for the recovery of Pd(II) in hydrochloric solution, *Bioresour. Technol.* 102 (2011) 3888–3893.
- [36] J.K. Bediako, S. Lin, A.K. Sarkar, Y. Zhao, J.W. Choi, M.H. Song, W. Wei, D.H.K. Reddy, C.W. Cho, Y.S. Yun, Benignly-fabricated crosslinked polyethylenimine/calcium-alginate fibers as high-performance adsorbents for effective recovery of gold, *J. Clean. Prod.* 252 (2020).
- [37] M. Sayin, M. Can, M. Imamoglu, M. Arslan, 1,3,5-Triazine-pentaethylenhexamine polymer for the adsorption of palladium (II) from chloride-containing solutions, *React. Funct. Polym.* 88 (2015) 31–38.
- [38] M. Sayin, M. Can, M. Imamoglu, M. Arslan, Highly efficient adsorption of Rh(III) from chloride containing solutions by triazine polyamine polymer, *Water Air Soil Pollut.* 228 (2017) 100.
- [39] M. Can, M. Doğan, M. Imamoglu, M. Arslan, Au (III) uptake by triazine polyamine polymers: mechanism, kinetic and equilibrium studies, *React. Funct. Polymers.* 109 (2016) 151–161.
- [40] A. Hao, S. Wang, J. Huang, Filling the pores of the post-cross-linked polymers with different rigid cross-linking bridges, *ChemistrySelect.* 5 (2020) 7941–7946.
- [41] R. Fan, F. Xie, X. Guan, Q. Zhang, Z. Luo, Selective adsorption and recovery of Au (III) from three kinds of acidic systems by persimmon residual based biosorbent: A method for gold recycling from e-wastes, *Bioresour. Technol.* 163 (2014) 167–171.
- [42] X. Li, C. Zhang, R. Zhao, X. Lu, X. Xu, X. Xia, C. Wang, L. Li, Efficient adsorption of gold ions from aqueous systems with thioamide-group chelating nanofiber membranes, *Chem. Eng. J.* 229 (2013) 420–428.
- [43] F. Alguacil, Adsorption of Gold(I) and Gold(III) Using Multiwalled Carbon Nanotubes, *Appl. Sci.* 8 (2018) 2264.
- [44] T. Ogata, Y. Nakano, Mechanisms of gold recovery from aqueous solutions using a novel tannin gel adsorbent synthesized from natural condensed tannin, *Water. Res.* 39 (2005) 4281–4286.
- [45] N.F. Abd Razak, M. Shamsuddin, S.L. Lee, Adsorption kinetics and thermodynamics studies of gold(III) ions using thioctic acid functionalized silica coated magnetite nanoparticles, *Chem. Eng. Res. Des.* 130 (2018) 18–28.
- [46] F.Q. An, M. Li, R.Y. Wu, T.P. Hu, J.F. Gao, Z.G. Yuan, Effective recovery of AuCl₄ using D301 resin functionalized with ethylenediamine and thiourea, *Hydrometallurgy* 169 (2017) 356–361.
- [47] W. Liu, P. Yin, X. Liu, X. Dong, J. Zhang, Q. Xu, Thermodynamics, kinetics, and isotherms studies for gold(III) adsorption using silica functionalized by diethylenetriaminemethylenephosphonic acid, *Chem. Eng. Res. Des.* 91 (2013) 2748–2758.
- [48] C. Huang, X. Xu, J. Ao, L. Ma, F. Ye, Z. Wang, L. Xu, X. Zhao, H. Ma, Selective adsorption, reduction, and separation of Au(III) from aqueous solution with amine-type non-woven fabric adsorbents, *Mater.* 13 (2020) 2958.
- [49] L. Fu, L. Zhang, S. Wang, G. Zhang, J. Peng, Selective recovery of Au(III) from aqueous solutions by nano-silica grafted with 4-(aminomethyl) pyridine, *J. Sol-Gel Sci. Technol.* 83 (2017) 467–477.
- [50] M. Zhao, Z. Huang, S. Wang, L. Zhang, Ultrahigh efficient and selective adsorption of Au(III) from water by novel Chitosan-coated MoS₂ biosorbents: performance and mechanisms, *Chem. Eng. J.* 401 (2020).
- [51] C. Wu, X. Zhu, Z. Wang, J. Yang, Y. Li, J. Gu, Specific recovery and in situ reduction of precious metals from waste to create MOF composites with immobilized nanoclusters, *Ind. Eng. Chem. Res.* 56 (2017) 13975–13982.