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Schiff Base Polymer and Its Reduced Derivative: Synthesis and Comparative Adsorption toward Cu(II)

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Abstract: Schiff bases are well-established as strong ligands for heavy metal ions due to their electron-rich nature. Herein, a Schiff base-derived adsorbent was facilely synthesized via polymerization of *p*-phenylenediamine and glutaraldehyde, followed by reduction, for efficient Cu(II) removal. SEM observations revealed uniform spherical particles with diameters ranging from 0.3 to 1.5 μm . FTIR analysis indicated the formation of imine linkages and their partial reduction during the hydrothermal treatment. TGA and acid-stability tests further demonstrated that the reduction treatment enhanced the stability of the polymer in acidic media, although its thermal stability decreased slightly. Batch adsorption experiments under varying pH, initial Cu(II) concentration, and contact time revealed that the poly-Schiff base and its reduced derivative exhibited maximum adsorption capacities of 138.30 and 234.17 $\text{mg}\cdot\text{g}^{-1}$, respectively, both achieving over 76% of their equilibrium capacities within 30 minutes. Comparative FTIR and XPS analyses before and after adsorption indicated that while the poly-Schiff base adsorbed Cu(II) mainly through electrostatic attraction and coordination, the reduced adsorbent additionally facilitated the reduction of Cu(II) to Cu(I), which thus enhanced its adsorption performance.

1 Introduction

Attributable to the tremendous demand for circuit boards, the consumption of copper

increase continuously^[1]. The discharge of wastewater containing copper ions has been increasing^[2-4]. The water contaminant by copper ion could aroused a series risk of environment and public health consequentially^[5, 6]. Hence, innovating efficient treatment to remove Cu from wastewater has become the urgent and imperative task for researcher in the environment recovery area.

At present, various effective techniques have been adopted for capturing Cu from contaminated water, including electrolysis^[7], ion-exchange^[8], reverse osmosis^[9], precipitation^[10] and adsorption and so forth. Among these technologies, adsorption has emerged as one of the most promising methods for treating wastewater containing low concentrations of Cu(II) because of its operational simplicity, environmental compatibility, relatively low cost, and potential for adsorbent regeneration ^[11]. It is generally believed that a desirable adsorbent with efficacy, low-cost and high capacity is crucial issue for practical adsorption^[12]. Diverse adsorbent materials and their adsorption process have been extensively studied^[13, 14]. Organic polymers with abundant variety of functional groups exhibited fine performance in Cu removal ascribed to functional surface and controllable active site^[14, 15]. According to previous research, the chelating groups, such as amine group, carboxyl group and sulfhydryl groups, is evidently effective for facilitating adsorption performance^[16]. The coordination ability of functional group is principally relied on the electronegativity of ligands atom.

Schiff base structure, originated by Hugo Schiff in 1864, was generated via nucleophilic addition reaction between carbonyl and amine. Owing to the facile and green preparation, high-sensitive and chemical activity, Schiff bases derivatives have found versatile applications in recent years across various fields, notably in biomedicine^[17, 18], organic catalysis^[19, 20], and environmental monitoring^[21, 22]. For wastewater treatment, Schiff base functionalized composites act as highly effective ligands for most heavy metal ions attributed to their strong electronegativity of imine bond^[23, 24]. In particular, the lone pair of electrons on the imine nitrogen atom can act as an electron donor during metal complexation. On basis of fluorophores of Schiff base complex, an assortment of Schiff base ligands has been developed as the probe for recognition and detection of

metal ion at low concentration ($<0.1\text{ M}$)^[25-27]. The aforementioned studies revealed the highly sensitive, stable, and rapid coordination of metal ions with Schiff bases, involving van der Waals forces, electrostatic interactions, and coordination bonding^[28]. Consequently, Schiff base composites were ideal candidate for adsorbent of metal ion^[29-32]. Nevertheless, several limitations of Schiff bases restrict their application in contaminant removal, encompassing potential leaching, low precursor utilization, and insufficient functional group density, ultimately diminishing their cost-effectiveness and adsorption capacity^[33, 34]. To address these problems, two main strategies that modify the molecular structure of Schiff base composites have been investigated: first is fabrication of Schiff base structure based on natural polymers^[35]. Chitosan, the most widely used natural polymer, is often utilized in the synthesis of Schiff bases, which function as adsorbents for a variety of pollutants^[36]. For example, Alhalili crosslink the (E)-4-((2-hydroxyphenylimino) methyl) benzaldehyde to form the Schiff base structure and further synthesize the MnFe_2O_4 /chitosan/Schiff base composite via condensation of -OH. The adsorption capacity of the composite for Zn(II) reached $289.86\text{ mg}\cdot\text{g}^{-1}$, implying its applicability in wastewater treatment^[37]. Liu et al. prepared a foam through crosslinking Schiff base structures composed of chitosan, oxidized cellulose, and amino-modified graphene oxide, which demonstrated high adsorption capacity and selectivity toward Allura Red and Orange G. The second is grafting or introducing Schiff base functional structure into stable matrix or framework with high surface area^[38]. Zhang et al. synthesized Schiff base silica aerogels to enhance the stability and inhibit the aggregation of Schiff bases. The findings suggested the improved reusability and performance of Schiff base in adsorption for Pb(II) ^[39]. Wu et.al combine the Schiff base with graphene oxide via attachment of covalent, showing the adsorption capability of $243.3\text{ mg}\cdot\text{g}^{-1}$ for Cr(VI) and reducing ability of Cr(VI) to Cr(III) ^[40]. The incorporation of Schiff base into functionalized metal-organic frameworks (MOFs) more significantly strength the interaction between MOFs and divalent heavy metal ion than that of trivalent heavy metal ion^[41, 42]. Despite extensive research on modifying Schiff bases to improve their adsorption properties, a strategic polymerization approach that leverages their inherent chemical structure to concurrently achieve high functional

group density and enhanced monomer utilization has garnered little attention. Furthermore, the influence of the nitrogen atom's chemical state—especially the conversion between imine and amine functional groups—on the adsorption process of divalent heavy metal ions has not been fully established.

Accordingly, this study aimed to synthesize poly-Schiff bases with a high density of functional groups via the reaction between aldehyde and aromatic amine monomers, while precisely controlling their chemical states. The adsorption performance of the resulting poly-Schiff bases and their reduced derivatives was systematically evaluated under varying pH, initial concentration, and contact time to optimize the parameters for Cu(II) removal. The adsorption mechanism for divalent heavy metal ions was elucidated by analyzing the adsorption behavior and the conversion in the chemical bonding of functional groups, particularly focusing on the valence state of nitrogen atoms, before and after adsorption. This work provides insights into enhancing the precursor utilization and adsorption capacity of synthetic Schiff bases.

2 Experiment

2.1 Materials

All chemicals were of analytical grade and used as received without further purification. *p*-Phenylenediamine (pPD), glutaraldehyde (GA), and sodium borohydride (NaBH₄) were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Hydrochloric acid (HCl), sodium hydroxide (NaOH), and anhydrous ethanol were obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Without special caution, de-ionized water was used throughout all experiments.

2.2 Preparation of Schiff base polymers

The Schiff base polymer nanoparticles were prepared by the precipitation and the following hydrothermal reduction. Briefly, 8 mM *p*-phenylenediamine was dissolved in 50 mL 1M HCl solution under ice bath with magnetically stirring. Subsequently, 20 mL glutaraldehyde solution at diverse concentration was mixed with *p*-phenylenediamine solution respectively to restrict the ratio of *p*-phenylenediamine to

glutaraldehyde (1:1, 1:2 and 1:5). Then 2 M NaOH was added dropwise to adjust the pH to 12 and initiate the polymerization. After 3 h agitating under N₂ atmosphere at constant temperature (4, 25, or 50 °C), the precipitates were obtained by filtration and washed with deionized water and anhydrous ethanol. The Schiff base polymer particles were freeze-dried at -75 °C for 12 h to prevent oxidation before further treatment. Thereafter the prepared particles were dispersed in 0.15 M NaBH₄ hydrate solution before sealed by Teflon reactor. The reactor was heated at 90 °C for 12 h in the oven to reduce the Schiff base polymer. Afterwards the resultant particles were also filtrated by 0.45 µm polyester membranes and washed by deionized water and ethanol before vacuum-dried at 50 °C for 12 h.

The synthetic Schiff base polymer was denoted as pSB(x)-y. Where x represented the molar ratio of *p*-phenylenediamine to glutaraldehyde (x = 1:0.5, 1:1 or 1:2) and y represented the reaction temperature (y=4, 25 or 50), while the hydrothermal resultant was named as pSB(x)-y-R.

2.3 Characterization

The investigation of surface morphology was implemented on a scanning electron microscopy (SEM), The Fourier transform infrared (FTIR) spectra of Schiff base polymer and its reduced derivative before and after Cu(II) adsorption were recorded on a Nicolas IS10 spectrophotometer (ThermoFisher Scientific Instruments) at resolution of 4 cm⁻¹ with wavenumbers from 4000 cm⁻¹ to 500 cm⁻¹. Thermal stability of Schiff base polymer and its reduced derivative were analyzed using a SDT650 Simultaneous Thermal Analyzer (TA Instruments). 200 mg Schiff base polymer and its reduced derivative were dispersed and stirred at 450 rpm in HCl solution (pH=2~5) for 4 h to assess their acidic resistance. The absorbance of filtration was determined by visible light spectrophotometer at 450 nm. The X-ray photoelectron spectroscopy (XPS) analysis was carried out on a K-Alpha 1063 with Al Kα X-ray as the excitation source.

2.4 Adsorption experiment

Primarily, the Cu(II) solution was prepared by anhydrous CuCl₂ and the concentration was determined by inductively coupled plasma (ICP) with the standard Cu(II) solution

as the reference. All batch adsorption experiment of Schiff base polymer and its reduced derivative were performed on a reciprocating shaker at 150 rpm under 30 °C. The covered polyethylene vials were filled with 50 mL Cu(II) solution with dispersing 25 mg adsorbents. the pH of Cu(II) solution was adjusted using 2 mol·L⁻¹ HCl or NaOH. As the contrast, the blank assay was implanted in identical condition only without adding adsorbent. The concentration of Cu(II) after adsorption was measured by ICP. The assessment of adsorption behaviors investigated via varying the pH, initial concentration, and contact time. Specifically, the Cu(II) solution was adjusted pH=2~7 to evaluate the effect of initial pH of solution. For isotherm investigation, the initial concentration of Cu(II) solution was differed from 48.6 to 795.3 mg·L⁻¹ at pH=5.5 for 4 h adsorption. The kinetic studies were conducted at and initial concentration of Cu(II) of 528.4 mg·L⁻¹ for 0~240 min adsorption. The adsorption capacity at any contact time (q_t) and quilibrium (q_e) were calculated as follows:

$$q_t = \frac{C_0 - C_t}{m} V \quad (I)$$

$$q_e = \frac{C_0 - C_e}{m} V \quad (II)$$

where C_0 and C_e (mg·L⁻¹) refer to the initial and equilibrium concentration of Cu(II) solution, respectively. C_t is the Cu(II) concentration in solution at time t (mg·L⁻¹), m gives the dry mass of adsorbent (g), and V relates the volume of solution (L).

3 Result and Discussion

3.1 Synthesis and characterizations

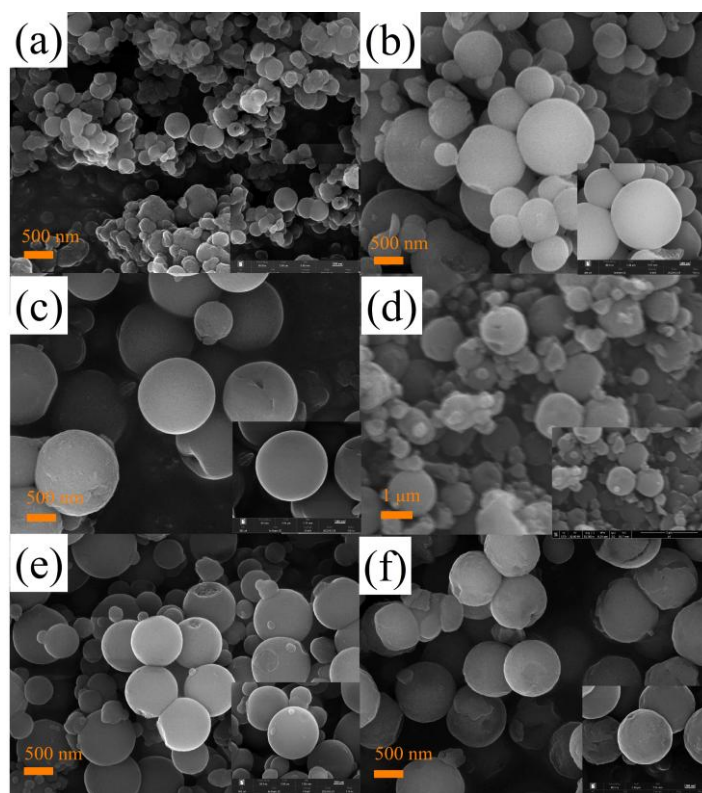


Figure 1. The SEM image of (a) pSB(1:1)-4; (b) pSB(1:1)-25; (c) pSB(1:1)-50; (d) pSB(1:2)-25; (e) pSB(1:5)-25; (f) pSB(1:2)-25-R. Right inset: the central magnification.

The morphology of SEM image of Schiff base polymer and its hydrothermal resultant was exhibited in figure 1. As is shown, the polymers generated by *p*-phenylenediamine and glutaraldehyde formed the even spheres ranging in size from 0.3 to 1.5 μm . Irregularly shaped micro fragments were observed, conjectured to arise from a comparatively lower degree of polymerization or incomplete particle growth. As temperature ascends, a concomitant augmentation in the average particle diameter occurred, coinciding with a concurrent reduction in fragmentary abundance. These morphological changes suggest that higher reaction temperatures promoted more complete polycondensation and particle growth by accelerating the reaction between the $-\text{NH}_2$ and $-\text{CHO}$ groups, as a result of more vigorous molecular collisions. The yield under divers temperature in Table 1 was consistent with the SEM image, providing additional evidence for the influence of reaction temperature. On the other hand, the

average diameter of Schiff base polymer particles obviously increased by proportionally raising the dosage of glutaraldehyde from 1:1 to 1:2. However, a further increase in the glutaraldehyde content to a molar ratio of 1:5 produced no substantial changes in the overall particle shape or surface morphology, suggesting that additional glutaraldehyde had only a limited effect on particle formation. Despite the theoretically same molar ratio of *p*-phenylenediamine and glutaraldehyde in reaction equation, the higher product yield and diameter of pSB(1:2)-25 suggested that excess glutaraldehyde was allowed conjugated into the molecular of Schiff base polymer as crosslinking reagent. Fig. 1f illustrated the unchanged size of pSB(1:2)-25-R compared with the Schiff base polymer. Nevertheless, the rough surface of particles was displayed in the product after hydrothermal reduction, presumably ascribed to the disintegration of the Schiff base polymer under excessively high temperature.

Table 1. Yield of pSB(1:1)-4, pSB(1:1)-25, pSB(1:1)-50, pSB(1:2)-25, pSB(1:5)-25 and pSB(1:2)-25-R

Sample	pS(1:1)-4	pS(1:1)-25	pS(1:1)-50	pS(1:2)-25	pS(1:5)-25	pS(1:2)-25-R
Yields /g	2.2821	2.3023	2.2521	2.3485	2.2301	2.2437
Yields	87.94	88.72	86.79	90.50	80.94	86.29

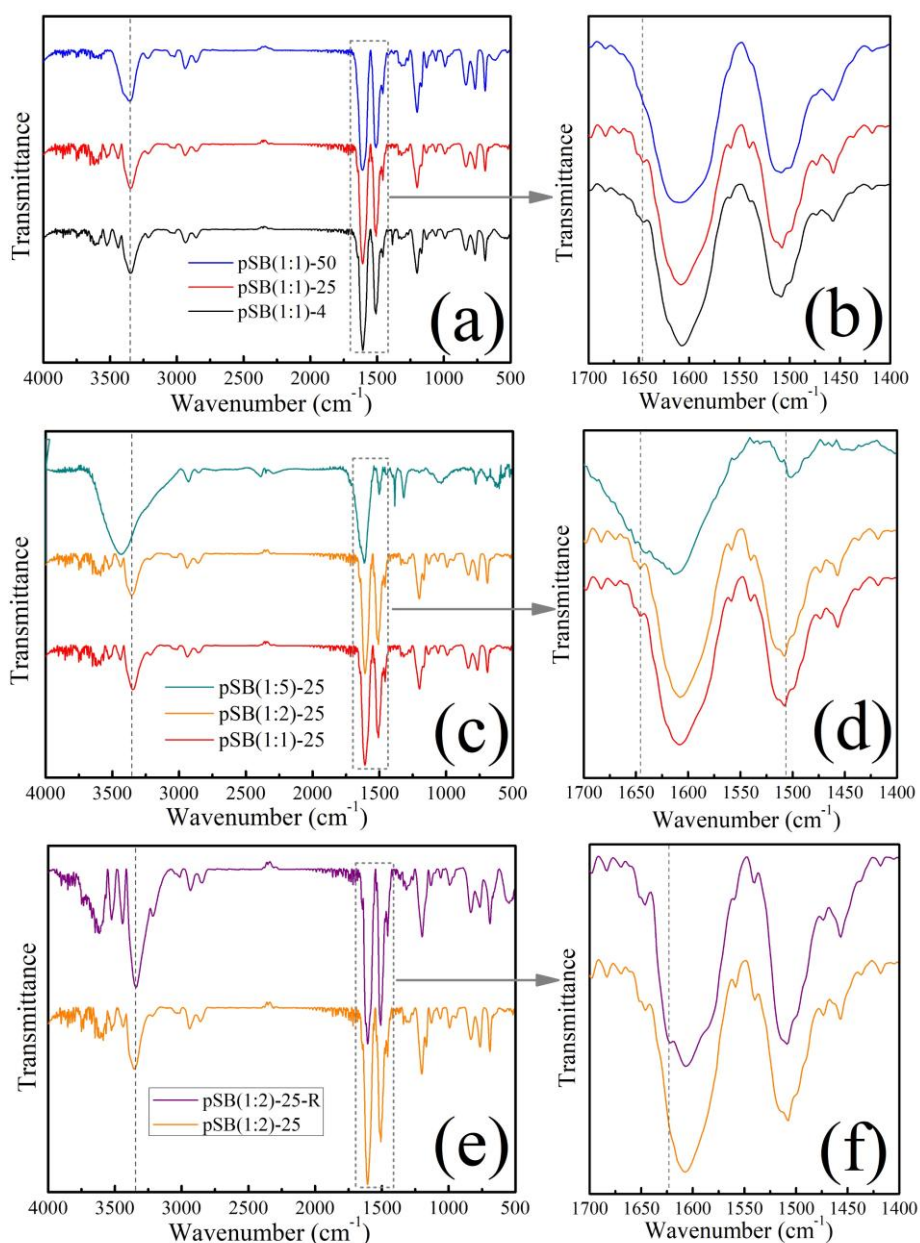
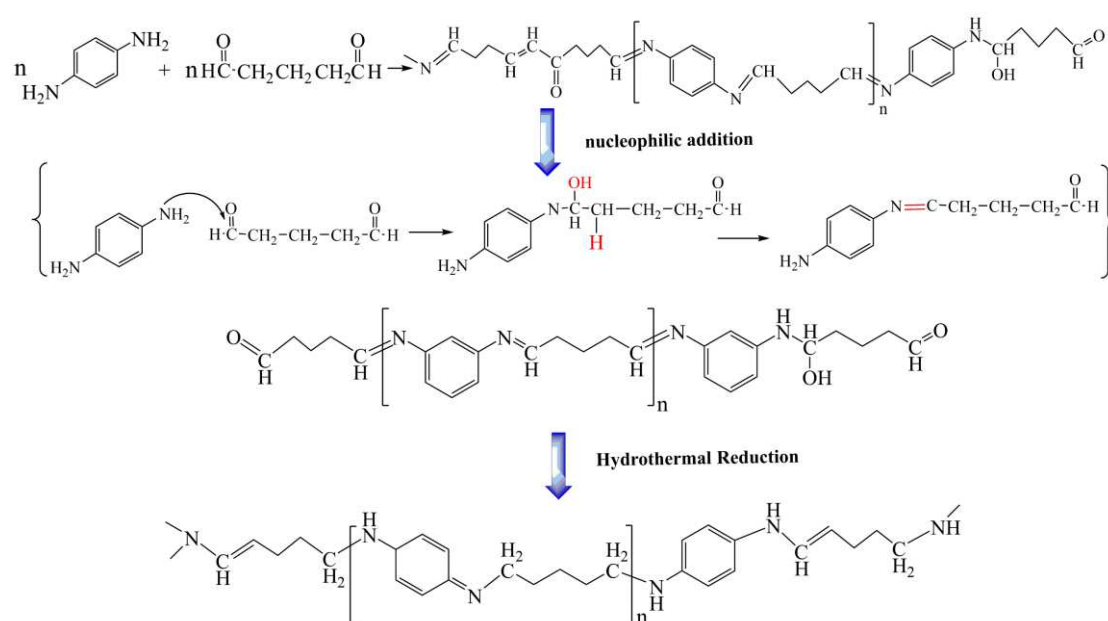


Figure 2. FT-IR spectra of Schiff base polymer at different temperatures (a); varying molar ratios of p-phenylenediamine to glutaraldehyde (c); and comparison with the reduced derivative (e). Panels (b), (d), and (f) are the magnified views of (a), (c), and (e), respectively, in the range of 1400~1700 cm^{-1} .

Figure 2a~2f present the FTIR spectra of Schiff base polymer under various conditions, together with a comparison with its reduced derivative. The adsorption located at 3300~3400 cm^{-1} was corresponding to N-H stretching vibration. Methylene C-H stretching vibrations arising from interaction with glutaraldehyde appeared at 2935 cm^{-1} and 2863 cm^{-1} . The implicit peak at 1650 cm^{-1} was attributed to unreacted aldehyde group. The two strong band at 1511 cm^{-1} and 1606 cm^{-1} were assigned to C=C

stretching vibration in the benzenoid amine structure, and C=N, resulting from reaction between aldehyde and amine group, respectively. The characteristic peak at 1625 cm^{-1} was the quinoid region. The FTIR results supported the formation of Schiff-base linkages through condensation between the amino groups of *p*-phenylenediamine and the aldehyde groups of glutaraldehyde, involving nucleophilic addition followed by dehydration, as illustrated in Scheme 1. The facilitation of addition at high temperature was validated by decreasing unreacted aldehyde and quinoid peak in pSB(1:1)-25 and disappearance in pSB(1:1)-50 (Figure 2a and 2b). As the feed amount of glutaraldehyde increased, the intensity of the characteristic peak corresponding to the aromatic-amine structure decreased (Figure 2c and 2d). This observation demonstrated that the proportion of amine functional groups could be tuned by altering the feeding amount of glutaraldehyde. Besides, the markedly increased intensity of the unreacted aldehyde-group peak and the blue-shifted N-H peak for pSB(1:5)-25 suggested that the C=N linkage failed to form in the presence of excess glutaraldehyde; instead, -OH group was generated, and its broad absorption masked the N-H peak. After hydrothermal reduction, the peak of quinoid was observed (Figure 2e and 2f). It revealed that the hydrothermal reduction process probably involves the reduction of the C=N bond by sodium borohydride, followed by subsequent oxidation induced by high temperatures, speculatively proposed in Scheme 1.



Scheme 1. Polymerization via nucleophilic addition and hydrothermal reduction

3.2 Stability

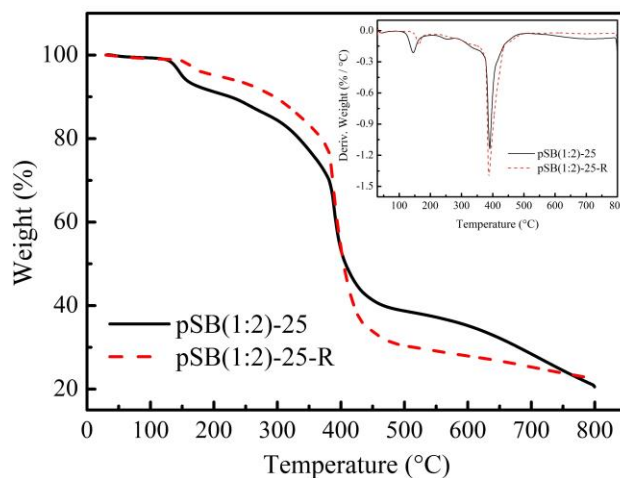


Figure 3. The thermogravimetry analysis curves of pSB(1:2)-25 and pSB(1:2)-25-R. Right inset: the Derivative thermogravimetry curves of pSB(1:2)-25 and pSB(1:2)-25-R.

The structure of the poly-Schiff base was further characterized by TGA analysis (Figure 3). Mass losses of 8.4% and 4.4% were observed before 200 °C for pSB(1:2)-25 and pSB(1:2)-25-R, respectively, which were ascribed to the evaporation of adsorbed moisture. The decomposition process occurred in two stages within the temperature range of 200~450 °C. The first gradual degradation occurred from 150 °C to 380 °C, corresponding to the breakdown of the polymer chain. In this stage, pSB(1:2)-25 experienced a mass loss of 7.0%, while pSB(1:2)-25-R experienced a mass loss of 11.9%. This infers that the degree of polymerization was scarcely affected after reduction. In the second stage, severe degradation occurred from 380 °C to 410 °C due to the cleavage of the aromatic skeleton. During this stage, pSB(1:2)-25 and pSB(1:2)-25-R exhibited mass losses of 39.8% and 66.0%, respectively. The markedly decreased thermal stability of pSB(1:2)-25-R indicates a reduction in bond energy, resulting from the partial conversion of the Ar–N=C structure to Ar–NH–C (benzenoid amine) during hydrothermal reduction. Furthermore, the almost identical residual mass weights of pSB(1:2)-25 and pSB(1:2)-25-R extrapolate the retention of the molecular chain and framework following the functional group conversion. This variability in thermal stability also demonstrates that the chemical state of nitrogen was successfully altered by hydrothermal reduction.

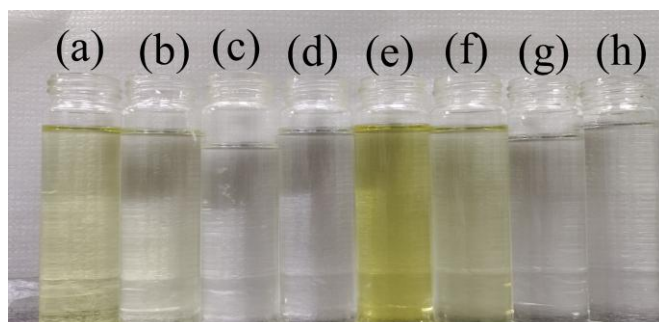


Figure 4. The filtrate chrominance of pSB(1:2)-25 and pSB(1:2)-25-R after stirring in HCl solution at various pH value. (a) pSB(1:2)-25-R for pH=2; (b) pSB(1:2)-25-R for pH=3; (c) pSB(1:2)-25-R for pH=4; (d) pSB(1:2)-25-R for pH=5, (e) pSB(1:2)-25 for pH=2; (f) pSB(1:2)-25 for pH=3, (g) pSB(1:2)-25 for pH=4, (h) pSB(1:2)-25 for pH=5.

The acidic stability was tested by measuring the dissolution of the sample in HCl solutions of varying concentrations. The colority variation of the filtrates is displayed in Figure 4, and the corresponding filtrate absorbance and mass loss of pSB(1:2)-25 and pSB(1:2)-25-R after stirring in HCl solutions with various pH values were summarized in Table 2. Compared to pSB(1:2)-25, pSB(1:2)-25-R exhibited a remarkably reduced mass loss in high-concentration HCl solutions at pH = 2 and pH = 3, with experimental mass loss decreased of 17% and 12%, respectively. The dissolution of Schiff base polymers is mainly attributed to the cleavage of polymer molecular chains. Specifically, the protonation and hydrolysis of C=N bonds broke the molecular skeleton, converting C=N groups into -CHO) and amine -NH- groups. Obviously, a higher ratio of quinoid structures to C=N-Ar linkages can effectively inhibit molecular chain cleavage. In addition, the negligible mass loss of pSB(1:2)-25 at pH = 5 suggested its excellent structural stability under near-neutral conditions.

Table 2. The filtrate absorbance and mass loss of pSB(1:2)-25 and pSB(1:2)-25-R after stirring in HCl solution at various pH value

Samples	pSB(1:2)- 25/ pH=2	pSB(1:2)- 25/ pH=3	pSB(1:2)- 25/ pH=4	pSB(1:2)- 25/pH=5	pSB(1:2)- 25-R /pH=2	pSB(1:2)- 25-R/pH=3	pSB(1:2)- 25-R/ pH=4	pSB(1:2)- 25-R/pH=5
Absorbance	0.178	0.089	0.061	0.052	0.288	0.185	0.092	0.073
Mass loss	19%	13%	6%	0.9%	36%	25%	13%	8%

Combined with molecular-structural analysis, the formation of benzenoid amine structures via hydrothermal reduction contributed to the improved acid stability of pSB(1:2)-25-R. Considering the acidic nature of PCB wastewater, this favorable acid

resistance ensured stable surface accessibility for practical adsorption applications.

3.3 Adsorption performance

3.3.1 Influence of pH on Cu(II) adsorption

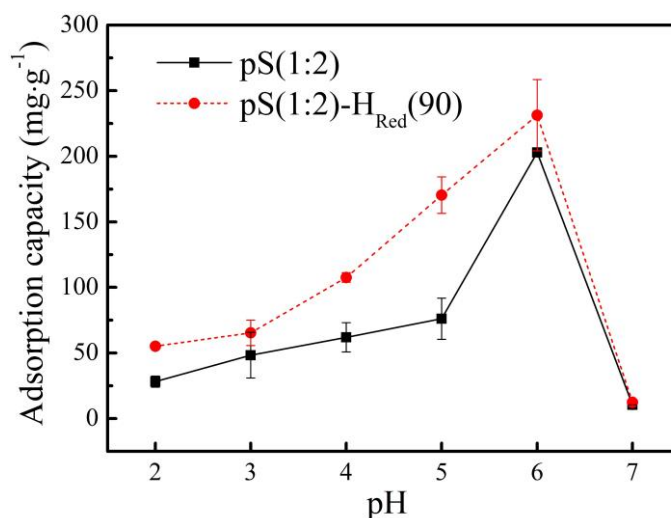
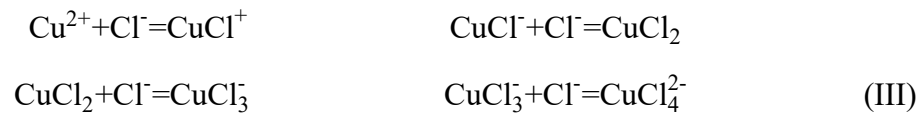


Figure 5. Effect of pH on Cu(II) adsorption by pSB(1:2)-25 and pSB(1:2)-25-R

The adsorption performance of adsorbents was significantly influenced by the concentration of protons due to alterations in the surface charge of the adsorbent. The effect of pH on the adsorption capacity of pSB(1:2)-25 and pSB(1:2)-25-R were investigated by varying the pH of the medium from 2 to 7. As illustrated in Figure 5, the adsorption capacities of both pSB(1:2)-25 and pSB(1:2)-25-R increased rapidly as the pH value rose from 2 to 6. For pSB(1:2)-25, a dramatic increase from 76.1 to 202.9 $\text{mg}\cdot\text{g}^{-1}$ was observed as the pH increased from 5 to 6, while a similar steep increase from 65.3 to 231.3 $\text{mg}\cdot\text{g}^{-1}$ was seen for pSB(1:2)-25-R from pH 3 to 6. The adsorption behavior of both pSB(1:2)-25 and pSB(1:2)-25-R was ascribed to the protonation of the C=N and –NH– groups, which occupied active sites and reduced adsorption capacity at lower pH levels. The higher electron density on the C=N group of pSB(1:2)-25 compared to the –NH– group of pSB(1:2)-25-R resulted in more facile protonation, leading to a lower adsorption capacity for pSB(1:2)-25 in highly acidic medium. The speciation of Cu(II) was also determined by the acidity of the medium. Extensive studies indicate that Cu(II) hydrolysis begins at approximately pH 6, producing CuOH^+ . Colloidal hydroxide formation is dominant at pH levels ranging from 6 to 12. In alkaline

solutions with $\text{pH} > 10$, $\text{Cu}(\text{OH})_3^-$ forms, and $\text{Cu}(\text{OH})_4^{2-}$ predominates in hydrolysate at $\text{pH} > 13$. Additionally, $\text{Cu}(\text{II})$ forms four consecutive complexes with Cl^- as follows:



These complexes were claimed to be different in electronic properties of surface, and have the impact on interaction between $\text{Cu}(\text{II})$ and adsorbent. In the medium with lower pH , the coordination between polymer ligand and $\text{Cu}(\text{II})$ was prevented by the CuCl_m^n ($m=1\sim 4$, $n=+1\sim -2$). When pH value increased, the hydrolysis of $\text{Cu}(\text{II})$ decrease the Cu^{2+} in solution and depress its diffusion to the surface of adsorbent. The formation of $\text{Cu}(\text{II})$ complex can further explain the effect of pH on adsorption performance of Schiff base polymer and reduced derivative. Concerned of the protonation of adsorbent and $\text{Cu}(\text{II})$ complex, the optimum pH was selected 5.5 in the successive experiment.

3.3.2 Initial concentration effect and adsorption isotherm

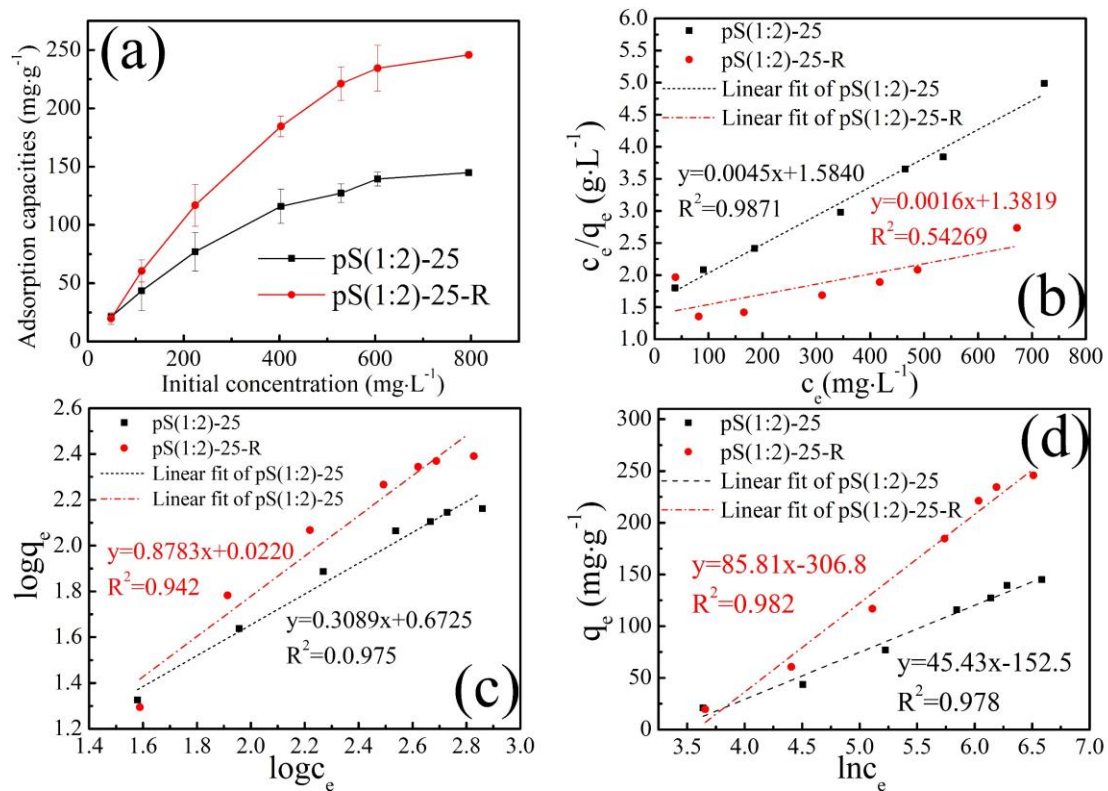


Figure 6. (a) Effect of initial concentration on $\text{Cu}(\text{II})$ adsorption by pSB(1:2)-25 and pSB(1:2)-25-R. Linear fitting of pSB(1:2)-25 and pSB(1:2)-25-R for the (b) Langmuir model, (c) Freundlich

model and (d) Temkin model

The effect of initial Cu(II) concentration on the adsorption behavior of Schiff base polymer(pSB(1:2)-25) and its reduced derivative (pSB(1:2)-25-R) was systematically investigated. Figure 6a depicts the saturated adsorption capacities of pSB(1:2)-25 and pSB(1:2)-25-R at varying initial Cu(II) concentrations. The adsorption capacities of both materials increased sharply when the initial Cu(II) concentration rose from 10 to 200 mg·L⁻¹. However, beyond 200 mg·L⁻¹, the increase in adsorption capacity plateaued. According to the Gibbs adsorption equation (Equation III), the concentration gradient serves as the critical driving force for the diffusion and transfer of adsorbate onto the adsorbent surface. At initial concentrations below 200 mg·L⁻¹, the lower concentration gradient at equilibrium resulted in insufficient occupation of active binding sites on the adsorbent. In contrast, at higher initial concentrations, the adsorption capacity tended to stabilize, which was attributable to the saturation of the adsorbent arising from the high concentration gradient.

$$\Gamma_{2(1)} = \Gamma_2 - \Gamma_1 \frac{c_2^\alpha - c_2^\beta}{c_1^\alpha - c_1^\beta} \quad (IV)$$

Where the $\Gamma_{2(1)}$ was the adsorption capacity in interface of phase. c_2^α , c_2^β , c_1^α , c_1^β were the concentration of solute and solvent in liquid and solid phase.

Experimental data for incrementally varied initial concentrations were analyzed using three common adsorption isotherm models to further explore the interaction between the adsorbent and Cu(II). The mathematical equations for the Langmuir, Freundlich and Temkin models are presented as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m} \quad (V)$$

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (VI)$$

$$q_e = B \ln A_T + B \ln C_e \quad (B = \frac{RT}{b_T}) \quad (VII)$$

where C_e (mg·L⁻¹) is the equilibrium concentration of Cu(II) solution, q_e (mg·g⁻¹) is the adsorption capacity at equilibrium, q_m (mg·g⁻¹) is the maximum adsorption capacity at saturation, while b (g·L⁻¹) correlates the isotherm constant for Langmuir model. K_f (mg·g⁻¹ (L·mg⁻¹)^{1/n}) and n represent the isotherm constants for Freundlich model. A_T

serves as the Temkin equilibrium binding constant, and b_T ($\text{J}\cdot\text{mol}^{-1}$) is the Temkin constant associated with the heat of adsorption. R ($8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$) and T (K) represent the universal gas constant and absolute temperature, respectively.

Simulation results of isotherm models were presented in Figure 6(b~d), and the corresponding calculated parameters were summarized in Table 3. The adsorption data of pSB(1:2)-25 were found to fit the Langmuir isotherm model better than other two model due to the strongest correlation ($R^2=0.987$). This observed behavior indicates that Cu (II) adsorption onto Schiff base polymers mainly follows a monolayer adsorption mechanism. Moreover, the comparable R^2 values (0.975 and 0.978) for the Freundlich and Temkin models demonstrate that multilayer adsorption coupled with chemical interactions exists on a small proportion of adsorption sites. The rapid crosslinking between glutaraldehyde and m-phenylenediamine accounts for this phenomenon: partial amino groups react with aldehyde groups without dehydration, retaining hydroxyl groups and expanding interchain spacing. The resultant loose structure and moderate porosity of polymer particles allow pronounced intraparticle diffusion of metal ions, which ultimately leads to the observed multilayer adsorption characteristic. In contrast to pSB(1:2)-25, the Temkin model provides a more accurate description of Cu(II) adsorption on pSB(1:2)-25-R. Data analysis reveals that chemical interactions between Cu(II) and the $-\text{NH}-$ and $\text{C}=\text{N}$ functional groups of pSB(1:2)-25- R^2 were governed predominantly by binding forces other than electrostatic attraction. As shown in Table 3, the relatively low correlation coefficient of Langmuir suggests a higher contribution of chemisorption after hydrothermal reduction with NaBH_4 . The $1/n$ values of both pSB(1:2)-25 and pSB(1:2)-25-R fall within the range of 0.1~1, confirming favorable adsorption characteristics. The maximum adsorption capacities of pSB(1:2)-25 and pSB(1:2)-25-R reached $138.30 \text{ mg}\cdot\text{g}^{-1}$ and $234.17 \text{ mg}\cdot\text{g}^{-1}$, respectively, demonstrating the excellent adsorption performance of both Schiff base polymer and its reduced derivative toward Cu(II). Notably, the adsorption capacity of pS(1:2)-25-R increased considerably by 69.3% compared with that of pS(1:2)-25, this enhancement was attributed to the partial conversion of imine ($\text{C}=\text{N}$) groups into secondary amine ($\text{C}-\text{NH}-\text{C}$) groups, which provided a more favorable chemical

environment for the binding of Cu(II).

Table 3. Adsorption isotherm parameters of Cu(II) on pSB(1:2)-25 and pSB(1:2)-25-R

Adsorption isotherm model	Parameters	pSB(1:2)-25	pSB(1:2)-25-R
Langmuir	q_m (mg·g ⁻¹)	223.7	628.9
	b (g·L ⁻¹)	0.00282	0.00115
	R^2	0.9871	0.5429
Freundlich	K_F (mg·g ⁻¹ (L·mg ⁻¹) ^{1/n})	2.036	1.052
	$1/n$	0.6725	0.8783
	R^2	0.9752	0.9425
Temkin	A_T (L·g ⁻¹)	0.0348	0.0280
	B (mg·g ⁻¹)	45.43	85.81
	R^2	0.9781	0.9817

3.3.3 Contact time effect and adsorption kinetics

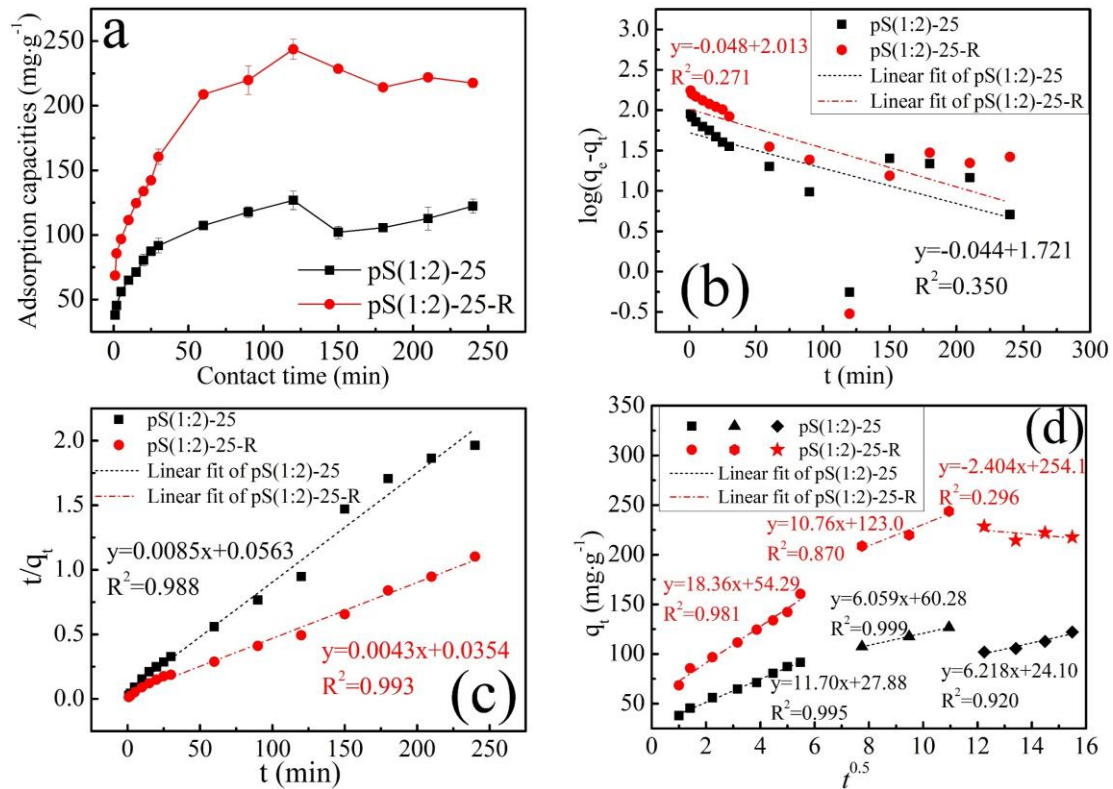


Figure 7. (a) Effect of contact time on Cu(II) adsorption onto pSB(1:2)-25 and pSB(1:2)-25-R.

TKinetic modeling for Cu(II) adsorption: (b) pseudo-first-order kinetic plots; (c) pseudo-second-order kinetic plots; (d) Weber-Morris intraparticle diffusion model plots.

The adsorption capacity of Cu(II) on both adsorbents exhibited a two-stage kinetic

process (Figure 7a). In the first stage, rapid physical and surface chemical adsorption occurred, actualizing 76% of the equilibrium adsorption capacity for pSB(1:2)-25 and 78% for pSB(1:2)-25-R, respectively, within the initial 30 minutes. The similar slopes of pSB(1:2)-25 and pSB(1:2)-25-R implies a comparable affinity for Cu(II) between the two materials. Subsequently, the rate of adsorption gradually decreased, reaching equilibrium within 3 hours. This stage is likely dominated by coordination with functional groups and intra-particle diffusion. Notably, pSB(1:2)-25-R exhibited a relatively higher adsorption rate in this period, which was ascribed to the stronger ligand interaction between the $-NH-$ group and Cu(II). Presumably, minor polymer decomposition in acidic solution accounted for the slight drop in adsorption capacity observed after 2 h.

Three kinetic models were applied to analyze the Cu(II) adsorption process on the Schiff base polymer and its reduced derivative: the pseudo-first order model and the pseudo-second order model, and the Weber and Morris intraparticle diffusion model. The linear equations of these models are expressed as follows:

pseudo-first order model

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (\text{VII})$$

pseudo-second order model

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (\text{VIII})$$

Weber-Morris intraparticle diffusion model:

$$q_t = k_{id} t^{0.5} + C \quad (\text{IX})$$

Where t (min) signifies the adsorption time, q_e ($\text{mg} \cdot \text{g}^{-1}$) is the equilibrium adsorption capacities, q_t ($\text{mg} \cdot \text{g}^{-1}$) denotes the adsorption capacity at t time, and k_1 (min^{-1}), k_2 ($\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$) are the adsorption rate constants, respectively. k_{id} defines the rate constant of intraparticle diffusion model while C represents the constant related to the surface properties of solid–liquid interface.

The fitting parameters for these models, derived from the data in Figure 7b–d, are listed in Table 4. Regression analysis revealed that the kinetic data for both adsorbents better fit the pseudo-second order model, as evidenced by higher correlation coefficients ($R^2=0.9882$ for pSB(1:2)-25 and $R^2=0.9938$ for pSB(1:2)-25-R). The theoretical q_e of

Schiff base polymer and its reduced derivative were 117.9 and 230.9 $\text{mg}\cdot\text{g}^{-1}$, showing satisfactory consistency with the experimental data (pSB(1:2)-25: 126.7 $\text{mg}\cdot\text{g}^{-1}$ and pSB(1:2)-25-R: 243.7 $\text{mg}\cdot\text{g}^{-1}$). The calculation demonstrated that pseudo-second order model precisely describes the Cu(II) adsorption on both adsorbents

Furthermore, the fitting results of the Weber-Morris intraparticle diffusion model in Figure 7d revealed that the adsorption of Cu(II) onto the two as-prepared adsorbents proceeded in three distinct stages. In the initial stage, Cu(II) ions were rapidly captured through boundary-layer diffusion driven by electrostatic attraction. The abundant accessible surface binding sites of the adsorbents contributed to this fast adsorption behavior. In the subsequent stage, the gradual occupation of active sites led to a noticeable decline in the adsorption rate. At this stage, the mass transfer of Cu(II) from the exterior surface to the internal structure of the adsorbents became the dominant process, accompanied by continuous binding interactions with polymer molecular chains. In the final stage, the adsorption curves of both samples gradually plateaued, suggesting that the adsorption system slowly reached thermodynamic equilibrium through chemical reaction interactions. Collectively, the linear fitting results of the intraparticle diffusion model verified that the Cu(II) adsorption process of the two poly-Schiff base adsorbents involved multiple synergistic interaction mechanisms.

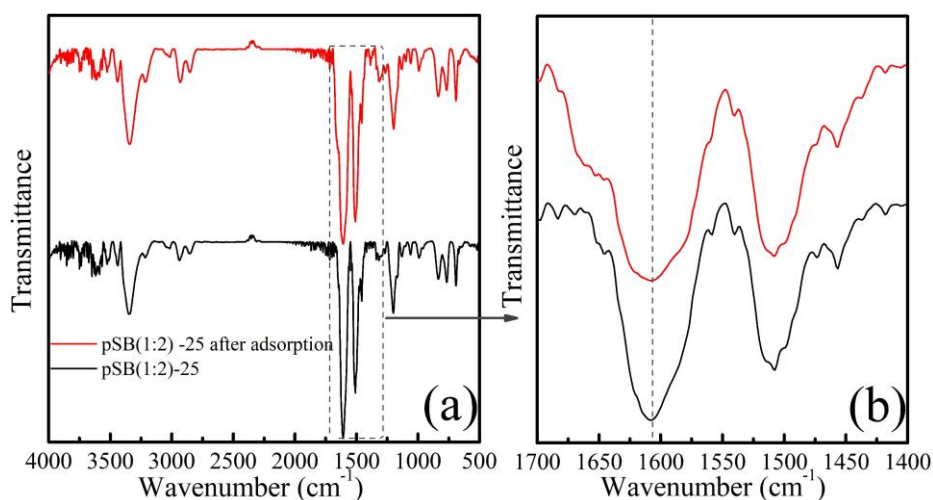
Significantly, pSB(1:2)-25-R exhibited a distinctly lower slope in the final diffusion stage than pristine pSB(1:2)-25, demonstrating its faster equilibrium attainment. This phenomenon indicated that the reduction of C=N groups effectively improved the chemisorption performance of the poly-Schiff base material toward Cu(II). By comparison, the loose particle-surface structure of pSB(1:2)-25 contributed to its relatively higher final-stage slope, which agreed well with the analytical results from adsorption isotherm models. Overall, the kinetic results indicate that Cu(II) adsorption by both materials involved a combination of external mass transfer, intraparticle diffusion, and interactions with accessible nitrogen-containing binding sites.

Table 4. The kinetic fitting parameters of pSB(1:2)-25 and pSB(1:2)-25-R for Cu(II) adsorption

Adsorption kinetic model	Parameter	pSB(1:2)-25	pSB(1:2)-25-R
pseudo-first order model	$q_{e, \text{exp}} (\text{mg} \cdot \text{g}^{-1})$	126.7	243.7
	$q_{e, \text{cal}} (\text{mg} \cdot \text{g}^{-1})$	52.6	103.1
	$k_1 (\text{min}^{-1})$	0.0101	0.0111
	R^2	0.350	0.271
pseudo-second order mode	$q_{e, \text{exp}} (\text{mg} \cdot \text{g}^{-1})$	126.7	243.7
	$q_{e, \text{cal}} (\text{mg} \cdot \text{g}^{-1})$	117.9	230.9
	$k_2 (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-1})$	1.277×10^{-3}	5.297×10^{-4}
	R^2	0.9882	0.9938
Intraparticles diffusion model	$k_{\text{id1}} (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})$	11.70	18.36
	$C_1 (\text{mg} \cdot \text{g}^{-1})$	27.88	54.28
	$k_{\text{id2}} (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})$	6.059	10.76
	$C_2 (\text{mg} \cdot \text{g}^{-1})$	60.28	123.0
	$k_{\text{id3}} (\text{mg} \cdot \text{g}^{-1} \cdot \text{min}^{-0.5})$	6.218	-2.404
	$C_3 (\text{mg} \cdot \text{g}^{-1})$	24.10	254.1

3.4 Adsorption mechanism

3.4.1 Schiff base polymer

**Figure 8.** FTIR spectra of pSB(1:2)-25 before and after Cu(II) adsorption: (a) full spectra, and (b) magnified view in the region of 1700~1400 cm^{-1} .

In the previously reported study, the mechanism of Cu(II) adsorption was primarily driven by electrostatic attraction between negatively charged groups and coordination with ligands. This electrostatic interaction in Cu(II) adsorption on both pSB(1:2)-25

and pSB(1:2)-25-R was substantiated by significant fluctuations in adsorption capacity with changes in initial pH value. Furthermore, the increase in pH value of the Cu(II) solution after adsorption corroborated these findings. However, due to the alteration of functional groups, it is predicted that the detailed adsorption mechanisms of Cu(II) on Schiff base polymer and its reduced derivative differ. Consequently, the interaction between Cu(II) and two synthesized adsorbents were further examined by comparing their chemical states and molecular structures before and after adsorption.

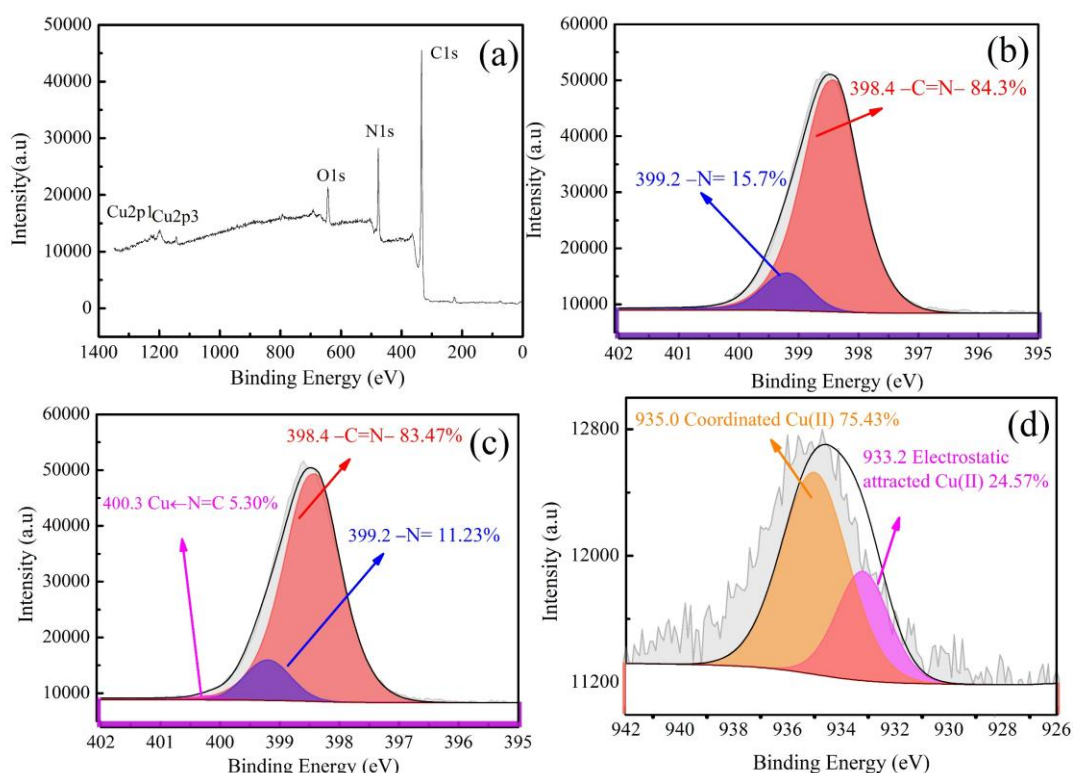
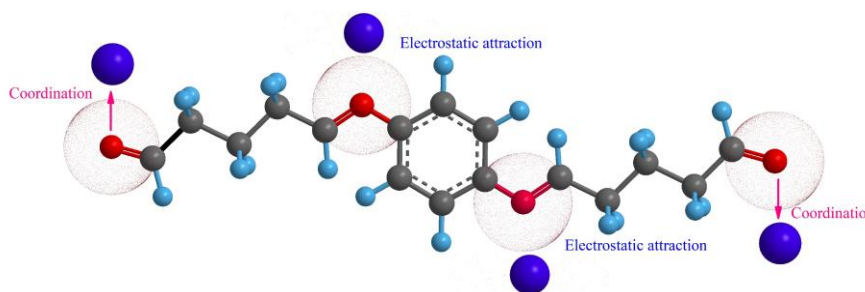


Figure 9. (a) XPS survey spectra of pSB(1:2)-25 after Cu(II) adsorption. High-resolution N 1s spectra of pSB(1:2)-25 before (b) and after (c) Cu(II) adsorption. (d) High-resolution Cu 2p_{3/2} spectrum on pSB(1:2)-25 after Cu(II) adsorption.

For pSB(1:2)-25, the FTIR spectrum revealed that the characteristic C=N stretching vibration at 1630 cm⁻¹ underwent a redshift to 1620 cm⁻¹ after Cu(II) adsorption, indicating a slight elongation of the C=N bond (Figure 8). This observation is consistent with the coordination of Cu(II) to the nitrogen atoms (Figure 9a). The survey spectrum confirmed the successful adsorption of Cu. Deconvolution of the N 1s region for the pristine pS showed two components: C=N (Schiff base, 398.4 eV, 84.3%) and -N= (quinoid imine, 399.2 eV, 15.7%) (Figure 9b). Following Cu(II) adsorption, the

proportions of these components decreased to 83.47% and 11.23%, respectively, while a new peak emerged at 400.3 eV (Figure 9c). This new component was assigned to N atoms involved in coordination with Cu(II). Furthermore, the Cu 2p_{3/2} spectrum was deconvoluted into two species: a major component at 935.0 eV (75.4%) attributed to coordinated Cu(II), and a minor component (24.6%) at a lower binding energy (933.2 eV) assigned to electrostatically attracted Cu(II) (Figure 9d). These results collectively validate that the adsorption of Cu(II) on pSB(1:2)-25 proceeds via a dual mechanism: initial electrostatic attraction to the negatively charged polymer surface, followed by specific coordination with the lone pair electrons on the nitrogen atoms of the C=N groups (Scheme 2).



Scheme 2. Proposed reaction mechanism of pSB(1:2)-25 during Cu(II) adsorption.

3.4.2 Reduction derivative

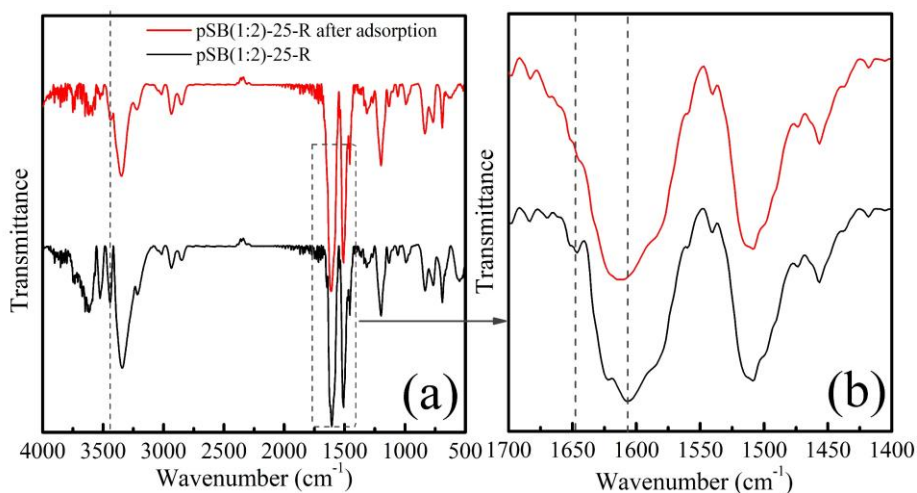


Figure 10. FTIR spectra of pSB(1:2)-25-R before and after Cu(II) adsorption: (a) full spectra, and (b) magnified view in the region of 1700~1400 cm⁻¹.

As shown in Figure 10, comparative analysis of the FTIR spectra of pSB(1:2)-25-R before and after Cu(II) adsorption revealed significant alterations in the polymer's chemical structure. These changes included a marked attenuation of the N-H

characteristic peak at 3480 cm^{-1} , suggesting the involvement of nitrogen atoms in coordinating with Cu(II) ions. Concurrently, the disappearance of the -CHO peak at 1650 cm^{-1} was conceivably attributable to an oxidation process induced by Cu(II). Furthermore, an obvious blue shift of the -C=N- absorption from 1606 cm^{-1} to 1640 cm^{-1} is observed, implicating its transformation into a quinoid imine structure (-N=).

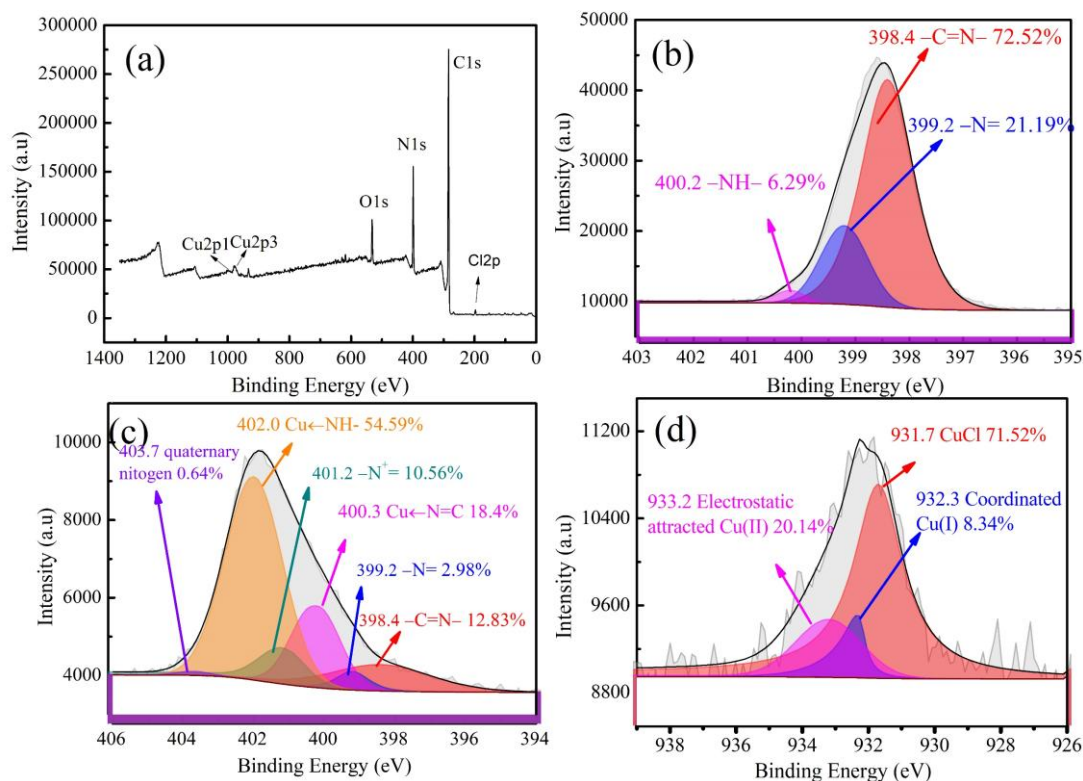
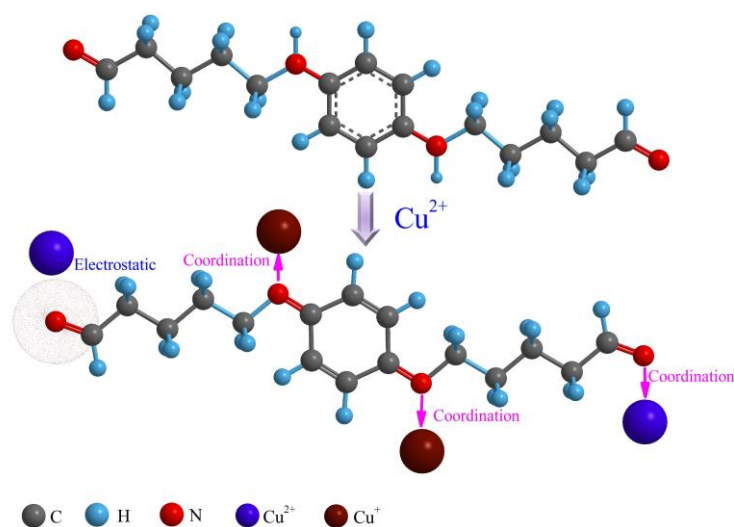


Figure 11. (a) XPS survey spectra of pSB(1:2)-25-R after Cu(II) adsorption. High-resolution N 1s spectra of pSB(1:2)-25-R before (b) and after (c) Cu(II) adsorption. (d) High-resolution Cu $2p_{3/2}$ spectrum on pSB(1:2)-25-R after Cu(II) adsorption.

The XPS survey spectrum confirmed the successful adsorption of Cu(II) onto pSB(1:2)-25-R, as evidenced by the emergence of characteristic Cu $2p_3$ and Cu $2p_1$ peaks (Figure 11a). High-resolution N 1s analysis provided insight into the adsorption mechanism. Prior to adsorption, the spectrum deconvoluted into three components: C=N (398.4 eV , 72.52%), $\text{-N}^+=$ (quinoid imine, 399.2 eV , 21.19%), and -NH- (aniline moiety, 400.2 eV , 6.29%) (Figure 11b). This profile indicated that NaBH_4 reduction partially converts C=N bonds to -CH-NH-Ar , while subsequent air oxidation readily converted some aniline units to the quinoid imine structure. After Cu(II) adsorption, the N 1s spectrum evolved into six components (Figure 11c): the proportions of C=N and $\text{-N}^+=$

decreased significantly to 12.83% and 2.98%, respectively, while a new peak at 400.3 eV, assigned to a C=N→Cu coordination complex, emerged and accounted for 18.4%. Of particular note, a dominant peak appeared at 402.0 eV, which arose from the coordination of –NH– to Cu (54.59 %). The peak at 401.2 eV (10.56%) arose from the protonation of quinoid imine, and a quaternary ammonium-salt component at 403.7 eV (0.64%) presumably stemmed from the adsorption of Cl[−] onto protonated –NH– groups. The chemical state of Cu on the polymer surface was analyzed via the Cu 2p_{3/2} spectrum (Figure 11d), which revealed three species: CuCl (931.7 eV, 71.52%), coordinated Cu(I) (932.3 eV, 8.34%), and uncomplexed Cu²⁺ (933.2 eV, 20.14%). Collectively, these results suggested that Cu(II) was not only adsorbed but also reduced on the pSB(1:2)-25-R surface, leading to the formation of CuCl deposited and the partial reduction of coordinated Cu(II) to Cu(I). This proposed mechanism was schematically illustrated in Scheme 3. The analysis of adsorption process, combined with the moderate improvement in the adsorption of Cu(II) on pSB(1:2)-25-R, indicated that the interaction between Cu(II) and the adsorbent was enhanced to a certain extent. This enhancement was presumably ascribed to the reduction of Cu(II) onto amine groups, which could provide additional binding sites.



Scheme 3. Proposed reaction mechanism of pSB(1:2)-25-R during Cu(II) adsorption.

4 Conclusion

A novel poly-Schiff base was synthesized via a facile and rapid synthetic strategy,

which exhibited high monomer utilization and dense surface functional groups for efficient Cu(II) removal from wastewater. For comparison, its reduced derivative was subsequently prepared through NaBH₄-assisted hydrothermal reduction to investigate the influence of the chemical state of nitrogen on adsorption performance. Characterization results revealed that the poly-Schiff base successfully formed uniform spherical particles through the nucleophilic addition reaction between p-phenylenediamine and glutaraldehyde, achieving a high polymerization degree. After reduction modification, the obtained adsorbent presented a rough surface morphology and typical quinoid-like structures. The adsorption behaviors of Cu(II) onto the original and reduced Schiff-base polymers closely followed the Langmuir and Temkin isotherm models, respectively, as well as the pseudo-second-order kinetic model. The maximum adsorption capacities reached 138.30 and 234.17 mg·g⁻¹ for the two adsorbents under optimal conditions. Solution pH was identified as the most critical factor dominating the Cu(II) adsorption process, because it significantly affected both the protonation degree of functional groups and the speciation of copper complexes. The as-prepared adsorbents, especially the reduced poly-Schiff base, possessed excellent acidic and thermal stabilities, demonstrating promising applicability for the treatment of printed circuit board (PCB) wastewater. Comparative mechanistic analysis confirmed that the superior adsorption performance of the reduced derivative was mainly attributable to the increased number of reductive functional sites.

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