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Regulation of interfacial properties of polybenzoxazine for effective removal of Cr(VI) from aqueous solution

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ABSTRACT

A novel polybenzoxazine for effective removal of Cr(VI) from aqueous solution has been fabricated by using inexpensive $CuCl_2$–melamine complex, bisphenol A and formaldehyde. In the curing process of benzoxazine monomer, different curing media can guide the directional distribution of functional groups of different polarity in the benzoxazine monomer, and thus can achieve the effect of regulating the interfacial properties of polybenzoxazine, and achieved an amine-rich surface and a suitable surface morphology by changing the monomer structure and the ratio of raw materials. This novel polybenzoxazine sorbent was characterized by using high-resolution scanning electron microscopy, energy dispersive spectrometer, Fourier transform infrared spectroscopy and thermogravimetric analysis. The experimental maximum removal efficiency for Cr(VI) was up to 96.7% and adsorption capacity was 116.32 mg/g at solution pH of 2 with temperature of 25°C. Langmuir model was successfully fitted with various curves obtained at different temperatures, and the kinetic data were well described by pseudo-second-order model. The novel polybenzoxazine absorbent promises such advantages as high removal efficiency, low cost, facile fabrication and good recycling performance.

Keywords: Polybenzoxazine; Interfacial properties; Regulation; Adsorption; Hexavalent chromium

1. Introduction

The existence of Cr(VI) in both natural water and industrial wastewater is a great potential hazard to the public health and ecological environment due to its high mutagenic and carcinogenic properties [1–3]. The recovery and treatment of Cr(VI) in industrial wastewater have aroused great concern. Currently, many treatment methods have been applied to remove Cr(VI) from wastewater, such as chemical reduction and precipitation, ion exchange, electrodialysis, reverse osmosis and adsorption [4–8]. Among them, adsorption is considered as one of the most effective methods to remove Cr(VI), with the advantages of simple equipment, low operating cost, recyclable metal ions, reusable adsorbent, etc.

Various adsorbents have been developed for the treatment of wastewater contaminated by Cr(VI), including activated carbons from different sources [9–12], biomass [13–16], synthetic polymers [17–20], agricultural wastes [21–23] and minerals [24,25], etc. Although activated carbon has a great advantage in adsorption capacity, the preparation requiring high-temperature calcination causes high energy consumption. Biosorbents with small adsorption capacity restricts its usage. Adsorbents from agricultural wastes are beneficial to green development, but it is difficult to collect them, and the pretreatment of adsorbent preparation has a very complicated process. Mineral adsorbents have limited use due to its low adsorption capacity, and may cause secondary contamination under acidic conditions. High-molecular polymer synthesized by chemical method can not only controllably prepare various novel adsorbents but also facilitate

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industrial production, rendering itself a potential effective adsorbent on the treatment of Cr(VI) contamination.

It has been reported that the amine-functionalized polymer adsorbents can much efficiently remove Cr(VI) from wastewater [26–28]. As amine groups can be easily protonated under acidic conditions, and Cr(VI) exists in the form of $HCrO_4^-$ in aqueous solution at a certain pH value, $HCrO_4^-$ and protonated amine group are rapidly combined by electrostatic interactions. Benzoxazine is a kind of thermosetting resin with advantage of low cost and high stability, and it is suitable for use in industrial production. In present study, a novel benzoxazine monomer enriched with amine groups was designed and synthesized, regulating its curing behavior by changing the curing media, hence a kind of polybenzoxazine adsorbent with rich amine groups on the surface and special morphology was obtained. Its removal efficiency of Cr(VI) in aqueous solution was found above 96% with high adsorption rate and large adsorption capacity, exhibiting excellent performance.

2. Materials and methods

2.1. Materials

Melamine (MA), $CuCl_2.2H_2O$, methanol, phenol (Ph), bisphenol A (BPA), formaldehyde, glycerol, silicone oil, hydrochloric acid (HCl) and potassium dichromate ($K_2Cr_2O_7$) were purchased from Sinopharm Group (Shanghai, China). All chemicals were used without further purification.

2.2. Preparation of the adsorbents

First, complex of copper and melamine (Cu–MA) was synthesized [29]. Then, a novel benzoxazine monomer was synthesized by utilizing this complex as amine source. Finally, different kinds of adsorbents were obtained by curing the synthesized benzoxazine monomers in different curing media. The preparation of the adsorbents requires three steps (as shown in Fig. 1), where @ represents complexation.

2.2.1. Synthesis of Cu–MA

The synthesis of complex of copper and melamine (Cu-MA) was done according to a study carried out by Chen et al. [29]. The typical synthetic procedure is shown as follows: 0.08 mol melamine and 0.04 mol $CuCl_2.2H_2O$ were added to a flask, followed by addition of 120 mL methanol, stirring in a water bath at 80°C for 4 h. After completion of the reaction, the mixture was allowed to cool to room temperature, filtered and washed the product twice with ether, dried in an oven, and grinded it into powder.

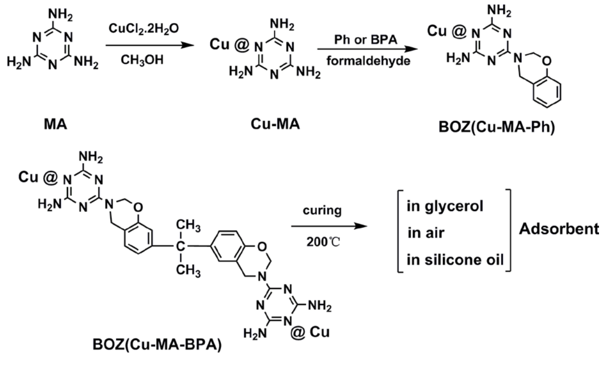


Fig. 1. Preparation of the adsorbents.

2.2.2. Synthesis of benzoxazine monomers

A mixture of methanol and water was used as the solvent (100 mL). 0.04 mol MA (Cu–MA), 0.015 mol bisphenol A and 0.06 mol formaldehyde were added, and then heated to 90°C reflux stirring reaction for 8 h. The mixture was allowed to cool to room temperature and the supernatant was removed. The product was washed with methanol to obtain benzoxazine monomer (denoted hereinafter as BOZ [Cu–MA–BPA]). A series of benzoxazine monomers were synthesized by changing the type and ratio of the reactants.

2.2.3. Preparation of polybenzoxazine adsorbents

The resulting benzoxazine monomers were cured in curing media such as glycerol, air and silicone oil at 200°C for 2 h, respectively. Among them, the product cured in glycerol was washed with water, whereas the products cured in silicone oil was washed with petroleum ether, then dried in an oven at 80°C to obtain polybenzoxazine adsorbents (denoted hereinafter as PBOZ [Cu–MA–BPA]).

2.3. Characterization

The PBOZ (Cu–MA–BPA) samples were characterized by Fourier transform infrared spectroscopy (FT-IR) (Thermo Fisher Scientific, Nicolet iS 50, USA). The sample and KBr powder were previously dried at 80°C for 4 h to ensure no moisture contained in the sample.

The thermogravimetric analysis (TGA) of PBOZ (Cu–MA–BPA) samples was carried out by thermogravimetric analyzer (NETZSCH, TG209C, Germany), rising from room temperature to 800°C at a heating rate of 10°C/min, and it was protected by filling nitrogen at a rate of 20 mL/min.

The PBOZ (Cu–MA–BPA) samples were characterized by high-resolution scanning electron microscopy (HRSEM) (Hitachi, SU8010, Japan) and X-ray energy dispersive spectrometer (EDS) (EDAX, Plus, USA) for the surface morphology and element composition. The water contact angle on the surface of PBOZ (Cu–MA–BPA) was measured by a contact angle tester (DataPhysics, OCA 15EC, Germany). The impact of curing media on the surface composition and morphology of polybenzoxazine was analyzed.

2.4. Adsorption experiments

The synthetic polybenzoxazine adsorbents were added to Cr(VI) acidic solution in a conical flask, the initial concentration of Cr(VI) ranged from 0 to 500 mg/L, the adsorption experiments were carried out in a water bath shaker with a constant temperature at the speed of 150 rpm until the adsorption equilibrium. The pH of the solution was adjusted with HCl. All the standard deviation in this study was calculated from the results of three parallel determinations. The equilibrium concentration of Cr(VI) is measured by atomic absorption spectroscopy (Thermo Fisher Scientific, ICE 3500, USA).

The equilibrium adsorption capacity (q_e, mg/g) is calculated by the following equation:

$$q_e = \frac{(C_0 - C_e) \times V}{m} \tag{1}$$

where C_0 and C_e (mg/L) represent the initial concentration and equilibrium concentration of Cr(VI) in the aqueous solution, respectively; V (mL) represents the volume of the solution and m (g) represents the dosage of adsorbent. The removal efficiency of Cr(VI) is calculated by the following equation:

$$\eta = \frac{(C_0 - C_e)}{C_0} \times 100\% \tag{2}$$

3. Results and discussion

3.1. Characterization of the adsorbents

Fig. 2 shows the FT-IR of the PBOZ (Cu–MA–BPA) adsorbent, and it can be found that the peak at 3,408 cm^{-1} is the O–H stretching vibration peak [30]; the peak at 3,320 cm^{-1} is mainly the –NH$_2$ vibration peak in the system [31]. The peak at 1,551 cm^{-1} should be the triazine ring aromatic C=N stretching vibration characteristic peaks in melamine, but the peak at 1,551 cm^{-1} is not obvious, indicating that Cu^{2+} may be complexed with N on the triazine ring of melamine during the synthesis of Cu–MA. The N–H stretching vibration peak is 1,655 cm^{-1} [30]. By contrast, the maximum amount of –NH$_2$ in the polybenzoxazine system was the product cured in glycerol as shown in Fig. 2(a), indicating that the product contains more free amine group. 750–810 cm^{-1} is the characteristic absorption peak of the substituent on the triazine ring, indicating that the ring-opening polymerization of benzoxazine monomer has happened. It can also be seen from Figs. 2(a) and (b) that the characteristic absorption peaks of benzoxazine rings are located at 950 and 1,240 cm^{-1} [32], indicating that the benzoxazines are not completely ring-opening polymerization in the curing medium glycerol and air, proving that the resulting product is indeed benzoxazine.

The TGA of the samples in Fig. 3 shows that they all have a high thermal stability, and 5 wt% weight loss temperature for the the samples cured in silicone oil and air are all above 280°C. These results further demonstrate that the synthetic product is a novel benzoxazine. The sample cured in glycerol has a certain weight loss at low temperatures, which may be attributed to the absorbing a certain amount of water in its purification process. The water on the sample is evaporated at relatively low temperature leading to its weight loss. Char yield for the sample, however, is above 40 wt%, suggesting that the sample is still a benzoxazine with high cross-linking density.

The HRSEM images of the PBOZ (Cu–MA–BPA) show that the samples obtained from three different curing media all have a three-dimensional block structure (Figs. 4 and S1) and different macroscopic morphology. We can see from Figs. S1(d)–(f) that all the three have microscopic accumulation of micropores in their interior. Among them, the benzoxazine cured in glycerol has a particle size of 1–2 μm, 5–10 μm in air, more than 10 μm in silicone oil. As we can see, the sample cured in glycerol medium was found to have smallest particle diameter and better dispersion. It indicates that the change of the curing media of benzoxazine monomers can directly regulate the morphology, particle diameter, degree of dispersion of polybenzoxazine. The results of the energy spectrum analysis are shown in Figs. 4(d)–(f), the surface of the samples obtained from three different curing media all contain C, N, O, Cl, Cu. As expected, the content of N on the surface of the product cured in glycerol and air is higher than that in silicone oil. It implies that glycerol is a polarized medium which can attract the polar groups –NH$_2$ in benzoxazine monomers, inducing the –NH$_2$ to the surface of the sample in the process of curing. The content of Cu element in PBOZ (Cu–MA–BPA) after being cured in three different curing media was relatively low, indicating that a large amount of Cu^{2+} mainly exist in the interior of polybenzoxazine.

The water contact angle on the surface of PBOZ (Cu–MA–BPA) in air was measured 96°, 140°, 150° (Fig. 5)

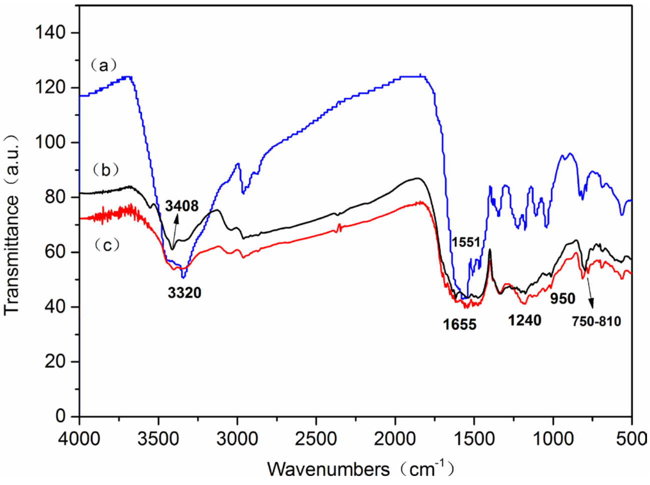


Fig. 2. FT-IR of PBOZ (Cu–MA–BPA) cured in (a) glycerol, (b) air and (c) silicone oil.

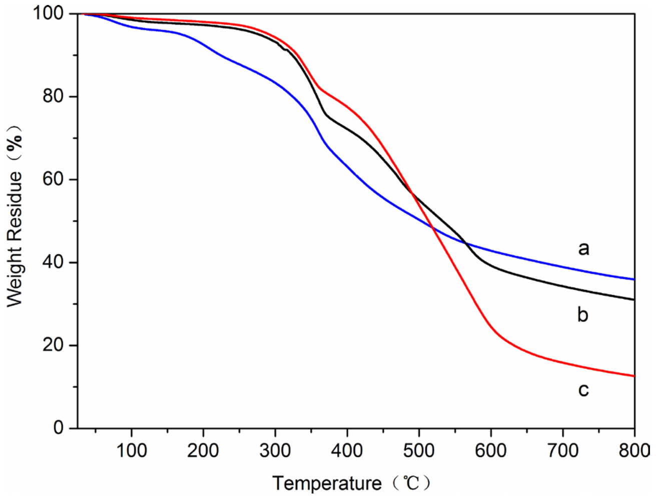


Fig. 3. TGA of PBOZ (Cu–MA–BPA) cured in (a) glycerol, (b) air, (c) silicone oil.

for the sample cured in glycerol, air and silicone oil medium, respectively. The size of the water contact angle on the solid surface is determined by the surface chemical composition and the roughness [13]. By contrast, it can be inferred that the surface of the sample cured in silicone oil contains more non-polar hydrophobic groups (benzene ring, methyl), while the sample cured in glycerol medium distributes more polar hydrophilic groups (–NH_2, –OH) on the surface.

3.2. Regulation of interfacial properties of polybenzoxazine

3.2.1. Effect of curing medium

The same benzoxazine monomer (MA [Cu–MA]: BPA:formaldehyde molar ratio 4:1.5:6) was cured at 200°C in glycerol, air and silicone oil medium, respectively. These samples were used as absorbents for the removal of Cr(VI) from aqueous solution. The results are shown in Fig. 6.

The adsorption capacity of Cr(VI) by polybenzoxazine cured in glycerol, air and silicone oil medium were 116.32, 86.36 and 28.79 mg/g, respectively (Fig. 6). It was obvious that the adsorption capacity of Cr(VI) by polybenzoxazine after being cured in glycerol was the best, followed by that in air, and that in silicone oil was the worst. The reason for this result can be explained by Fig. 7.

There are many free amine groups in the benzoxazine monomer as shown in Fig. 1, which is intentionally

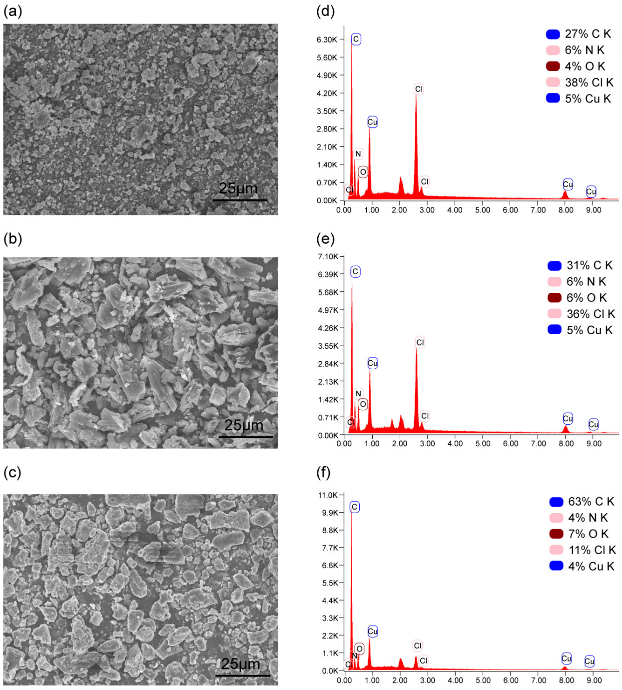


Fig. 4. HRSEM images and EDS of PBOZ (Cu–MA–BPA) cured in (a, d) glycerol, (b, e) air and (c, f) silicone oil.

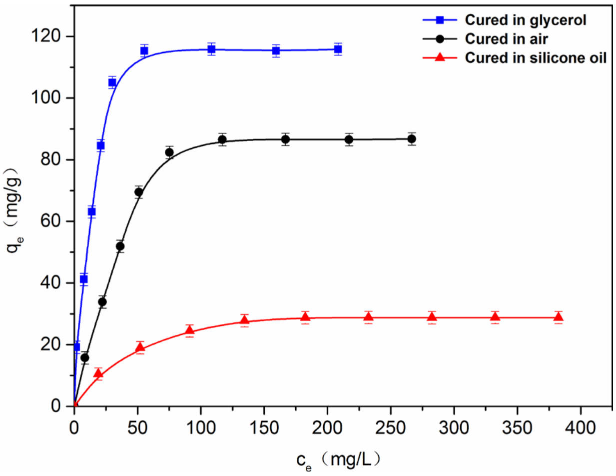


Fig. 6. Effect of curing medium on the adsorption of Cr(VI) by polybenzoxazine.

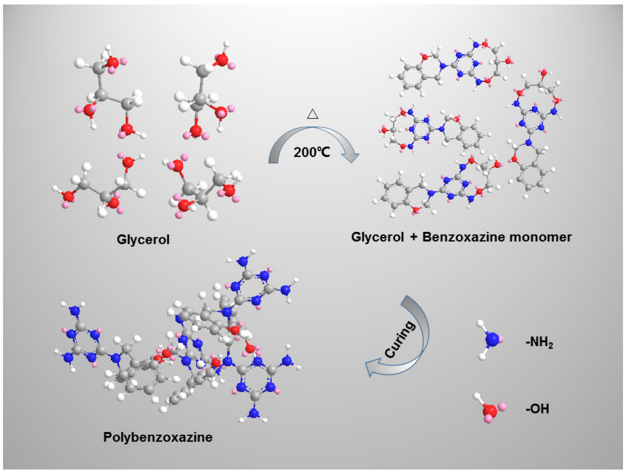


Fig. 7. Illustration of the regulation of interfacial properties of polybenzoxazine by curing medium.

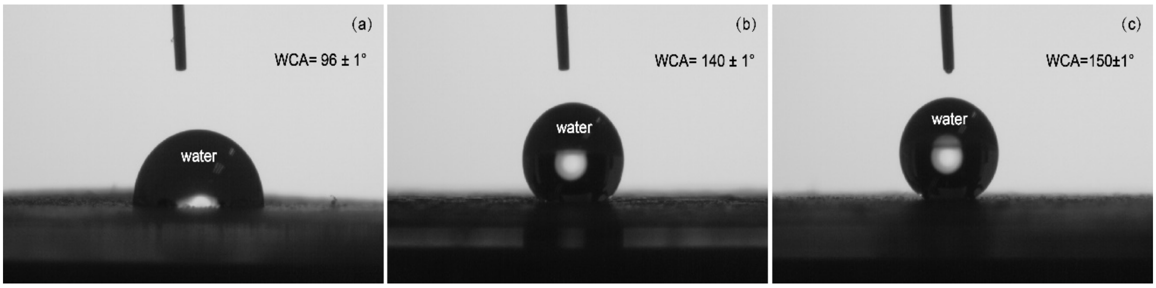


Fig. 5. Water contact angle on the surface of PBOZ (Cu–MA–BPA) in air cured in (a) glycerol, (b) air, (c) silicone oil.

designed in the raw material ratio. At the time of curing in the glycerol medium, the hydroxyls of glycerol have strong interaction with the amine groups of benzoxazine monomers. During the curing process, the amine groups of benzoxazine were attracted to the solid surface to form an amine-rich interface due to the salvation of glycerol, which has been proved by the characterization results of Figs. 4(a) and (d). According to the literature, the more amine groups on the surface of the adsorbent, the stronger its ability to adsorb Cr(VI) [33]. When curing in non-polar silicone oil medium, in order to reduce the Gibbs free energy of the system, the larger polar groups in the benzoxazine monomer (especially free amine group) spontaneously formed intermolecular or intramolecular hydrogen bonds, and gathered into a polar group inward, non-polar group outward micellar structure. The sample in silicone oil gets the minimum amine groups on the surface (shown in Fig. 4(f)) with weakest adsorption capacity of Cr(VI). The effect of the resulting absorbent cured in air falls between glycerol and silicone oil. The polybenzoxazines used in the following investigation were all obtained by curing in glycerol medium at 200°C.

3.2.2. *Effect of benzoxazine monomer and the ratio of raw materials*

Fig. 8 shows that effect of molar ratio of raw materials on the adsorption of Cr(VI) by polybenzoxazine based on Cu–melamine and bisphenol A.

It can be seen from Fig. 8 that the adsorption capacity of Cr(VI) by polybenzoxazine is increasing with the increase of the molar ratio of melamine and formaldehyde when the amount of bisphenol A is given. While the molar ratio of melamine and formaldehyde is fixed, the amount of bisphenol A has little effect on the adsorption capacity. This is because formaldehyde can easily react with amine group (–NH_2) to produce –$N(CH_2OH)_2$ according to the Mannich reaction mechanism, and then reacts with the active H on ortho-position or para-position of the phenol, intermolecular removal of H_2O to produce benzoxazine. The higher the molar ratio of melamine and formaldehyde, the more free –NH_2 benzoxazine on the surface, the more –NH_2 on the surface of polybenzoxazine after being cured, the higher adsorption capacity of Cr(VI) by the sample. However, too high molar ratio of melamine and formaldehyde will reduce the cross-linking degree of the formed polybenzoxazine, leading to a decrease in its acid resistance.

The adsorption capacity of Cr(VI) by various polybenzoxazines from different benzoxazine monomers are summarized in Fig. 9. By comparison, bisphenol A-based polybenzoxazine has a better adsorption capacity of Cr(VI) than that of phenol-based one, because of better reactivity of bisphenol A than phenol. Moreover, bisphenol A-based benzoxazine possesses longer monomolecular chain compared with phenol-based benzoxazine. Thus bisphenol A-based polybenzoxazine exhibits stronger acid resistance in the process of adsorption and improves the adsorption capacity. The benzoxazine synthesized with Cu–MA as the amine resource has a better adsorption capacity than that synthesized with pure melamine. This may be attributed to the novel synthesized benzoxazine monomer that has a suitable structure that is beneficial to improve the adsorption efficiency, and the number of free amine groups contained in the monomers of Cu–MA is higher than that of pure melamine. Therefore, the effect of $CuCl_2$ on the adsorption of Cr(VI) by samples requires further study.

3.2.3. *Effect of $CuCl_2$*

To confirm the effect of $CuCl_2$ on the adsorption of Cr(VI) by samples, the same amount of $CuCl_2$ was added to the system of adsorbent synthesis in three different ways under the identical other conditions to fabricate different samples. First, the sample PBOZ (Cu–MA–BPA) was made from Cu–MA complex, bisphenol A and formaldehyde, without adding $CuCl_2$ during the adsorption process. Second, the sample PBOZ (Cu–MA–BPA) was fabricated by above methods, but the same proportion of $CuCl_2.2H_2O$ was added during the adsorption process. Third, the sample PBOZ (BOZ [MA–BPA] + $CuCl_2$) was prepared by the BOZ (MA–BPA) monomer and $CuCl_2$. The adsorption of

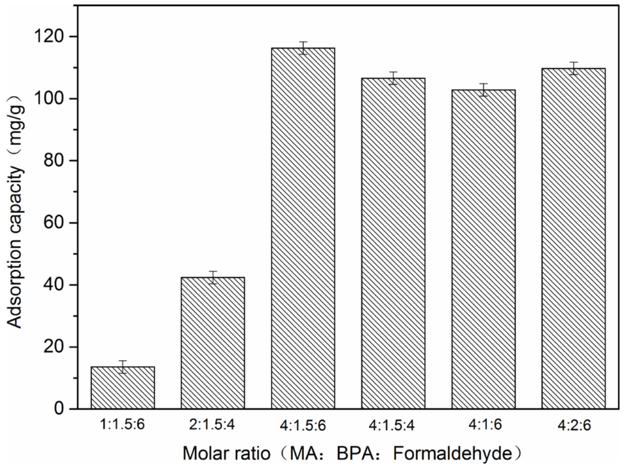


Fig. 8. Effect of the ratio of raw materials on the adsorption of Cr(VI) by PBOZ (Cu–MA–BPA).

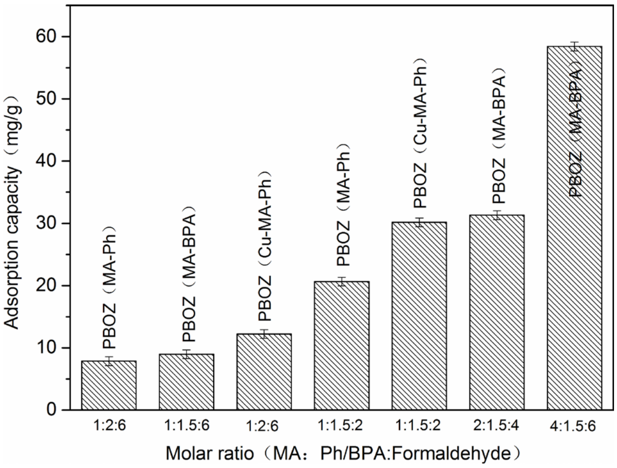


Fig. 9. Effect of benzoxazine monomers on the adsorption of Cr(VI) by PBOZ.

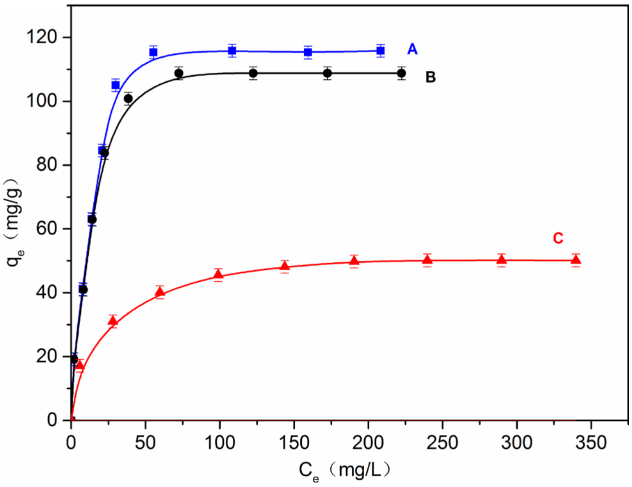


Fig. 10. Effect of $CuCl_2$ on the adsorption of Cr(VI) by polybenzoxazine. (A) PBOZ (Cu–MA–BPA), (B) PBOZ (Cu–MA–BPA) + $CuCl_2$ and (C) PBOZ (BOZ [MA–BPA] + $CuCl_2$).

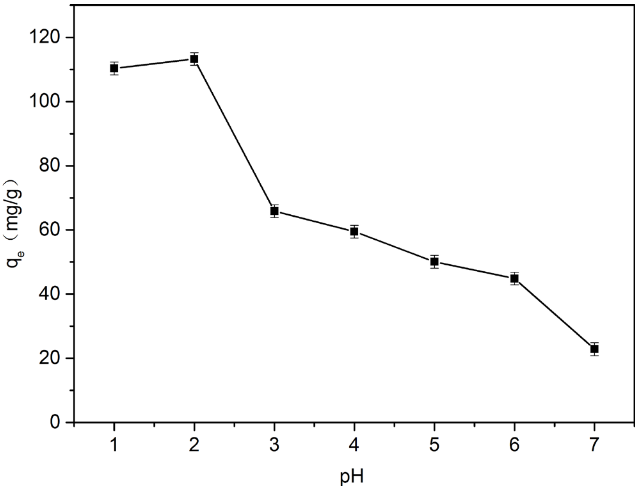


Fig. 11. Effect of pH on the adsorption of Cr(VI) by polybenzoxazine (adsorbent dosage, 0.1 g; volume, 50 mL; initial concentration, 250 mg/L; contact time, 5 h; temperature, 25°C).

Cr(VI) by three samples is shown in Fig. 10. By comparison, it can be seen that the adsorption capacity of Cr(VI) by the sample PBOZ (Cu–MA–BPA) is the best (Fig. 10(A)) among three tested samples. The result can be explained. It has been reported previously that Cu^{2+} reacts with N on the triazine ring of melamine to form an approximate planer structure of Cu–melamine complex [29], and it also can be proved by X-ray diffraction analysis results (Fig. S2). The polybenzoxazine based on the approximate planer amine source can improve the distribution of free amine groups on its surface, thus enhancing the adsorption capacity of Cr(VI) by the polybenzoxazine.

It is obvious that the adsorption capacity was significantly reduced by using the sample PBOZ (BOZ [MA–BPA] + $CuCl_2$) as absorbent (C). This may be attributed to the introduction of Cu^{2+} to the BOZ (MA–BPA) makes more amine groups in the BOZ combined with Cu^{2+} during curing process, the effective binding sites of Cr(VI) adsorbed by the polybenzoxazine adsorbent are reduced, thus reducing the adsorption capacity. It can be seen that a slight decrease in the adsorption capacity by using the sample PBOZ (Cu–MA–BPA) + $CuCl_2$ as absorbent. This may be because the introduction of Cu^{2+} may compete for partial substitution of H^+ to complex with amine group during the adsorption process [34].

The above experimental results show that different types of benzoxazine monomers can be controllably prepared by changing the synthesis conditions. Among them, the effect of polybenzoxazine on the adsorption of Cr(VI) by curing the benzoxazine monomer in glycerol at 200°C with MA (Cu–MA):BPA:formaldehyde molar ratio of 4:1.5:6 was the best, and the adsorption capacity can reach 116.32 mg/g. Therefore, the adsorbents used in the subsequent studies were prepared by the aforesaid conditions.

3.3. Effective removal of Cr(VI) by PBOZ (Cu–MA–BPA)

3.3.1. Effect of pH

As shown in Fig. 11, when the pH of the solution increases from 1 to 2, the adsorption capacity increases; when the pH of the solution increases from 2 to 7, the adsorption capacity decreases. The maximum adsorption capacity was achieved at pH of 2. This may be attributed to the pH value that can not only affect the existing form of Cr(VI) in the solution (Fig. 12), which more often exists in the form of $HCrO_4^-$ between pH 2 and 6, but also affect the protonation degree of amine groups on the surface of polybenzoxazine. Cr(VI) mainly exists in the form of $HCrO_4^-$ at pH of 2, which can be effectively adsorbed by positively charged protonated amine group on the adsorbent by electrostatic attraction (as shown in Fig. 13). When the pH of the solution increases from 2 to 7, the adsorption capacity decreases, which may be attributed to the increase of pH reducing the concentration of H^+ in the solution, resulting in a decrease in the protonation of the amine groups on the surface of the polybenzoxazine, thus weakening the adsorption capacity of $HCrO_4^-$. When the pH value of the solution is lower than 2, Cr(VI) exists more often in the form of H_2CrO_4, which cannot be adsorbed by the adsorbent.

The adsorption capacity depends on the pH value, indicating that electrostatic attraction and ion exchange play a very important role in the adsorption of Cr(VI) [35]. Here, $-NH_3^+$ and $HCrO_4^-$ were taken as an example, and the adsorption mechanism could be explained as follows:

$$\text{PBOZ–NH}_3^+ + \text{HCrO}_4^- \rightarrow \text{PBOZ–NH}_3^+\text{------HCrO}_4^-$$

$$\text{PBOZ–NH}_3^+\text{Cl}^- + \text{HCrO}_4^- \rightarrow \text{PBOZ–NH}_3^+\text{HCrO}_4^- + \text{Cl}^-$$

With the decline of the pH value, the protonation degree of the amine group increased, resulting in the increase of the adsorption capacity. According to the data of adsorption isotherm (Fig. 15) and adsorption model fitting (Table 1), we can see that the adsorption of Cr(VI) by polybenzoxazine is a single-layer chemical adsorption on the surface of the adsorbent, which accords with Langmuir isothermal adsorption model. Therefore, the above adsorption theory and the effect of pH on the adsorption performance can better explain the adsorption of Cr(VI) by polybenzoxazine.

3.3.2. Effect of the adsorbent dosage on the removal efficiency

Effect of the polybenzoxazine adsorbent dosage on Cr(VI) removal efficiency (initial concentration, 40 mg/L; volume, 50 mL; pH, 2; contact time, 5 h; temperature, 25°C) is shown in Fig. 14.

With the increase of the adsorbent dosage from 0.025 to 0.2 g/50 mL, the removal efficiency of Cr(VI) was enhanced rapidly from 34.7% to 96.7% (Fig. 14), and the effect is shown in the inset image of Fig. 14. It may be attributed to the increase of the adsorbent dosage, the adsorbents can provide more active sites [36], offering more chances for Cr(VI) to contact with the active sites of the adsorbent. When the adsorbent dosage increased from 0.1 to 0.2 g/50 mL, the removal efficiency increased 6.8% merely. Therefore, the optimal dosage of adsorbent used to adsorb Cr(VI) should be 0.1 g/50 mL.

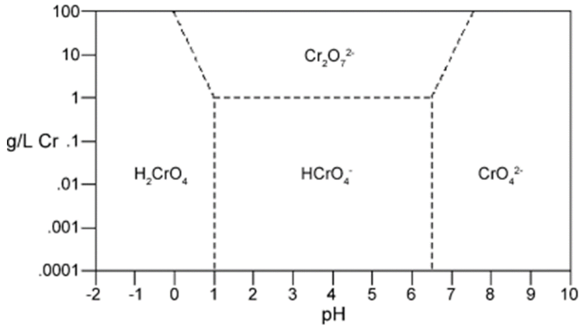


Fig. 12. Existing form of Cr(VI) under different pH values.

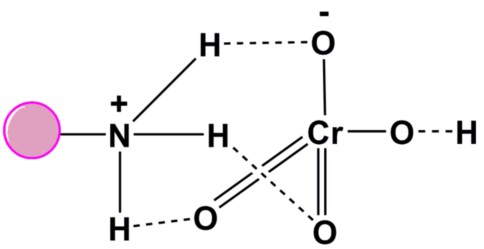


Fig. 13. Mechanism of adsorption of Cr(VI) by protonated amine group.

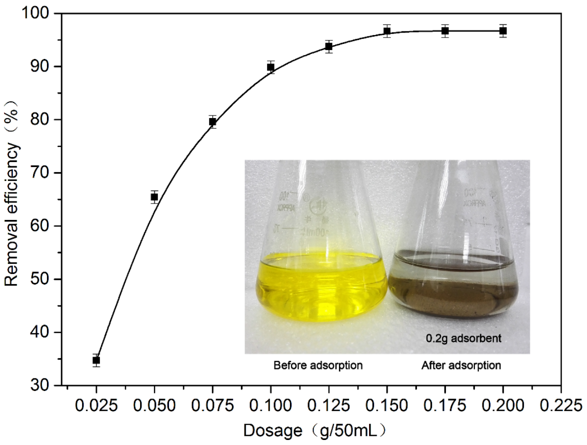


Fig. 14. Effect of the dosage on the removal efficiency of Cr(VI).

3.3.3. Adsorption isotherms

To investigate the effect of initial concentration of Cr(VI) ions on the equilibrium adsorption capacity of the absorbent at different temperatures, the adsorption isotherms of Cr(VI) adsorbed by polybenzoxazine at 25°C, 35°C, 45°C and 55°C were shown in Fig. 15. It is apparent that the adsorption capacity was decreased with increasing temperature suggesting that the adsorption process was exothermic. To better understand the adsorption behavior and mechanism, the equilibrium data of Cr(VI) adsorbed on the polybenzoxazine was fitted with the Langmuir (Eq. (3)) and Freundlich (Eq. (4)) models [37].

$$\frac{C_e}{q_e} = \frac{1}{q_m k_L} + \frac{1}{q_m} \times C_e \tag{3}$$

where C_e (mg/L) and q_e (mg/g) represent the Cr(VI) concentration and adsorption capacity at equilibrium, respectively. q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the equilibrium constant related to adsorption energy.

$$\ln q_e = \ln k_F + \frac{1}{n_F} \times \ln C_e \tag{4}$$

C_e (mg/L) and q_e (mg/g) are described as above, k_F and n_F are the isotherm constants which indicate the capacity and intensity of the adsorption, respectively.

As we can see from Table 1, where q_m (mg/g) is the maximum adsorption capacity and K_L (L/mg) is the equilibrium constant related to adsorption energy, k_F and n_F are the isotherm constants which indicate the capacity and intensity of the adsorption, R^2 values are all more than 0.968 in the Langmuir model, and these R^2 values are much higher than those of Freundlich model (0.856–0.883) at five different temperatures. The maximum adsorption capacity of Cr(VI) was 121.95 mg/g described by the Langmuir model, which was

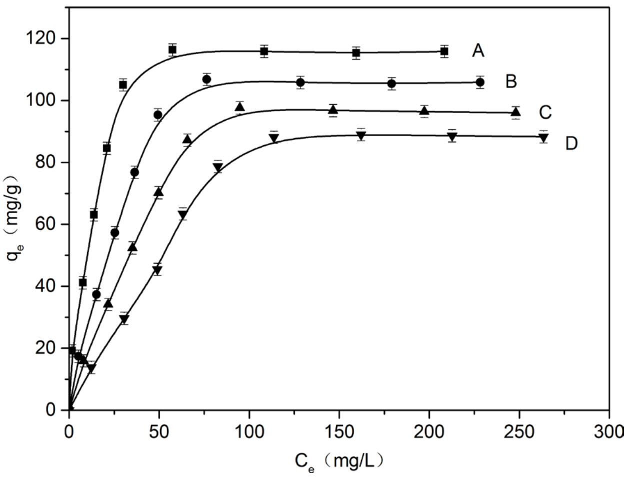


Fig. 15. Adsorption isotherms of Cr(VI) by polybenzoxazine at different temperatures of 25°C (A), 35°C (B), 45°C (C) and 55°C (D) (adsorbent dosage, 0.1 g; volume, 50 mL; pH, 2; contact time, 5 h).

Table 1
Adsorption isotherm parameters obtained from the Langmuir and Freundlich models

Temperature (°C)	Langmuir model			Freundlich model		
	q_m	K_L	R^2	k_F	n_F	R^2
25	121.95	0.109	0.997	21.43	2.71	0.861
35	114.94	0.066	0.993	11.06	2.12	0.856
45	107.53	0.045	0.987	7.12	1.89	0.865
55	105.26	0.025	0.968	3.78	1.61	0.883

closer to the experimental adsorption capacity (116.32 mg/g) compared with Freundlich model. Therefore, the Langmuir model could better represent the isothermal adsorption process for Cr(VI). Based on the assumption of Langmuir model, the adsorption process is a monolayer adsorption, and adsorption occurs on the surface of polybenzoxazine.

Thermodynamic parameters such as standard Gibbs free energy change (ΔG_m^0), standard enthalpy change (ΔH_m^0) and standard entropy change (ΔS_m^0) were calculated by the following equations [38]:

$$\Delta G_m^0 = -RT\ln K_a^0 \tag{5}$$

$$\ln K_a^0 = -\frac{\Delta H_m^0}{RT} + \frac{\Delta S_m^0}{R} \tag{6}$$

where R and T represent the molar gas constant (8.314 J mol^{-1} K^{-1}) and the temperature (K), respectively. K_a^0 represents the thermodynamic equilibrium constant, that is, the ratio of equilibrium adsorption capacity and equilibrium concentration of Cr(VI) ($K_a^0 = q_e/c_e$). K_a^0 for the adsorption process is calculated by plotting $\ln(q_e/c_e)$ vs. q_e and extrapolating to zero q_e. ΔG_m^0 can be calculated by Eq. (5). ΔH_m^0 and ΔS_m^0 values were calculated from the slope and intercept of the linear equations obtained by the linear relationship graphs of $\ln K_a^0$ and $1/T$ (Fig. 16), respectively.

The thermodynamic parameters are shown in Table 2. All the ΔG_m^0 values were negative (–0.32 to –6.16 kJ mol^{-1}), indicating that the adsorption of Cr(VI) by polybenzoxazine was a favorable process at thermodynamics. This result is consistent with the reported adsorption of Cr(VI) by a solid adsorbent [39,40]. ΔH_m^0 of the adsorption reaction was –66.28 kJ mol^{-1}, the negative ΔH_m^0 indicated that the adsorption reaction of Cr(VI) by polybenzoxazine was an exothermic process. Therefore, a relative low temperature was more suitable for the adsorption of Cr(VI), and this study was carried out at room temperature. ΔS_m^0 value was also negative, indicating that Cr(VI) has a low degree of freedom in the solid/solution interface during the adsorption, which was an entropy decreasing process.

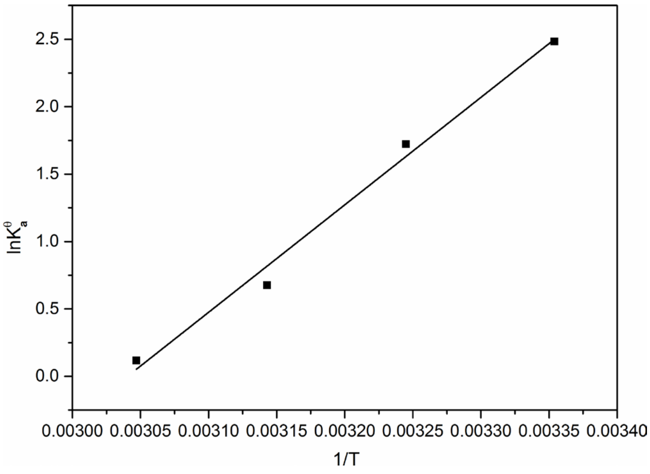
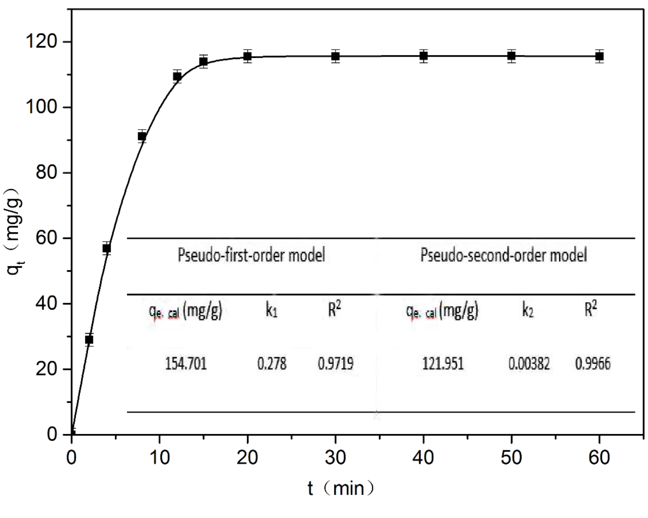


Fig. 16. Van't Hoff plot of the adsorption of Cr(VI) by polybenzoxazine.

Table 2
Thermodynamic parameters of the adsorption of Cr(VI) by polybenzoxazine adsorbent

ΔG_m^0 (kJ/mol)				ΔH_m^0 (kJ/mol)	ΔS_m^0 (kJ/mol)
298.15	308.15	318.15	328.15		
–6.16	–4.41	–1.79	–0.32	–66.28	–0.202



Pseudo-first-order model			Pseudo-second-order model		
$q_{e,cal}$ (mg/g)	k_1	R^2	$q_{e,cal}$ (mg/g)	k_2	R^2
154.701	0.278	0.9719	121.951	0.00382	0.9966

Fig. 17. Effect of contact time on the adsorption of Cr(VI) by polybenzoxazine (initial concentration, 250 mg/L; volume, 50 mL; adsorbent dosage, 0.1 g; pH, 2; temperature, 25°C).

3.3.4. Adsorption kinetics

Cr(VI) could be rapidly adsorbed by polybenzoxazine, and it almost achieved the adsorption equilibrium after 20 min (Fig. 17). This may be attributed to the fact that amine group (–NH$_2$) on the surface of the polybenzoxazine was rapidly protonated under acidic conditions, and then combined with the $HCrO_4^-$ by electrostatic attraction and ion exchange reaction.

In these adsorption experiments, the pseudo-first-order model (Eq. (7)) and the pseudo-second-order model (Eq. (8)) were employed to simulate the adsorption experimental data [40]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{7}$$

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{8}$$

where q_e and q_t (mg/g) represent the adsorption capacity at equilibrium and time t; k_1 (min^{-1}) and k_2 (g/(mg min^{-1})) refers to the pseudo-first-order rate constant and pseudo-second-order rate constant, respectively. The final fitted results are shown in Fig. 17, and the corresponding kinetic parameters of the two models are shown in the inset table of Fig. 17. It can be seen that the correlation coefficient (R^2) of the pseudo-second-order model is 0.9966, which is higher than that of the pseudo-first-order model ($R^2 = 0.9719$), and the pseudo-second-order model fitted to calculate the theoretical adsorption capacity ($q_{e,\text{cal}}$ (mg/g) = 121.95) is closer to the experimental adsorption capacity (116.32 mg/g). These results show that pseudo-second-order model is a good description of adsorption data of Cr(VI) adsorbed by polybenzoxazine.

3.4. Reusability

Reusability is one of the most important factors in the application of adsorbents. According to the decrease of the adsorption capacity of Cr(VI) by polybenzoxazine with the increase of pH, we could use the alkaline solution to elute and regenerate the adsorbent. Therefore, the regeneration experiments of the adsorption of Cr(VI) by polybenzoxazine were carried out with 0.1 mol/L NaOH solution. As shown in Fig. 18, the desorption efficiency were all about 95% after the Cr(VI) ions were desorbed from polybenzoxazine by NaOH. In addition, the adsorption capacity of Cr(VI) by polybenzoxazine is slightly decreased after five adsorption–desorption. This may be attributed to the loss of material during the adsorption–desorption cycle with NaOH destroying the chemical structure of the adsorbent, such as the functional groups on the surface of polybenzoxazine are weakened, etc.

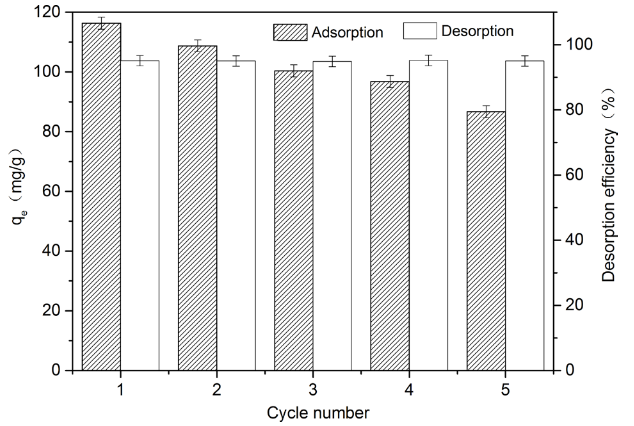


Fig. 18. Performance of polybenzoxazine by five adsorption–desorption cycles of generation. (Adsorption conditions: adsorbent dosage, 0.1 g; volume, 50 mL; initial concentration, 250 mg/L; pH, 2; contact time, 1 h; temperature, 25°C. Desorption conditions: eluent, 0.1 mol/L NaOH solution; volume, 50 mL; contact time, 1 h; temperature, 25°C.)

4. Conclusion

A novel adsorbent for effective removal of Cr(VI) from aqueous solution was fabricated by using an inexpensive, stable polybenzoxazine with facile large-scale production. The interfacial properties of the polybenzoxazine are regulated by changing the curing medium, the monomer structure and the ratio of raw materials to achieve the amine-rich surface and the small particle diameter. The results indicate that the novel adsorbent achieves a maximum adsorption capacity of 116.32 mg/g and a maximum removal efficiency of 96.7% at pH of 2 and temperature of 25°C. Isotherm studies demonstrate that the Langmuir model better fits the experimental data compared with Freundlich isotherm. The adsorption kinetics follows the pseudo-second-order model. In conclusion, the novel polybenzoxazine was first applied to remove Cr(VI) from aqueous solutions with high removal efficiency and adsorption capacity, promising to be an effective adsorbent for the removal of Cr(VI) from aqueous solutions.

Acknowledgments

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Support information

In order to characterize the impact of $CuCl_2.2H_2O$ in the synthesis of Cu–MA and the novel benzoxazine monomer, we carried out X-ray diffraction analysis of the materials (D8 Advance, Bruker, Germany).

As shown in Figs. S2(a)–(c), the X-ray diffraction peaks of $CuCl_2.2H_2O$ are at 16°, 22° and 45°–60°, and melamine appeared between 15° and 30°. The formation of Cu–MA did not show the X-ray diffraction characteristic peak of $CuCl_2.2H_2O$, indicating that the addition of $CuCl_2.2H_2O$ fully reacts with melamine. Then, a new diffraction peak appeared between 10° and 15°, which is better illustrated by the formation of Cu–MA. Cu–MA also exhibited diffraction peaks between 25° and 30°, corresponding to the peak position of melamine, indicating the melamine over dosage for the purpose to allow $CuCl_2.2H_2O$ fully involved in the formation of Cu–MA reaction.

From Figs. S2(d)–(f), we can see that benzoxazine cured in glycerol has no apparent characteristic peak in the position of $CuCl_2.2H_2O$, melamine, Cu-MA, while clear peaks at 30° occurred at the time of being cured in air and in the silicone oil. The comparison shows that the acid resistance of the benzoxazine increased after being cured and the particle diameter decreased, which is conducive to the adsorption. It is consistent with the experimental results of the adsorption of Cr(VI), that is, the benzoxazine monomer cured in glycerol achieved the best adsorption capacity of Cr(VI).

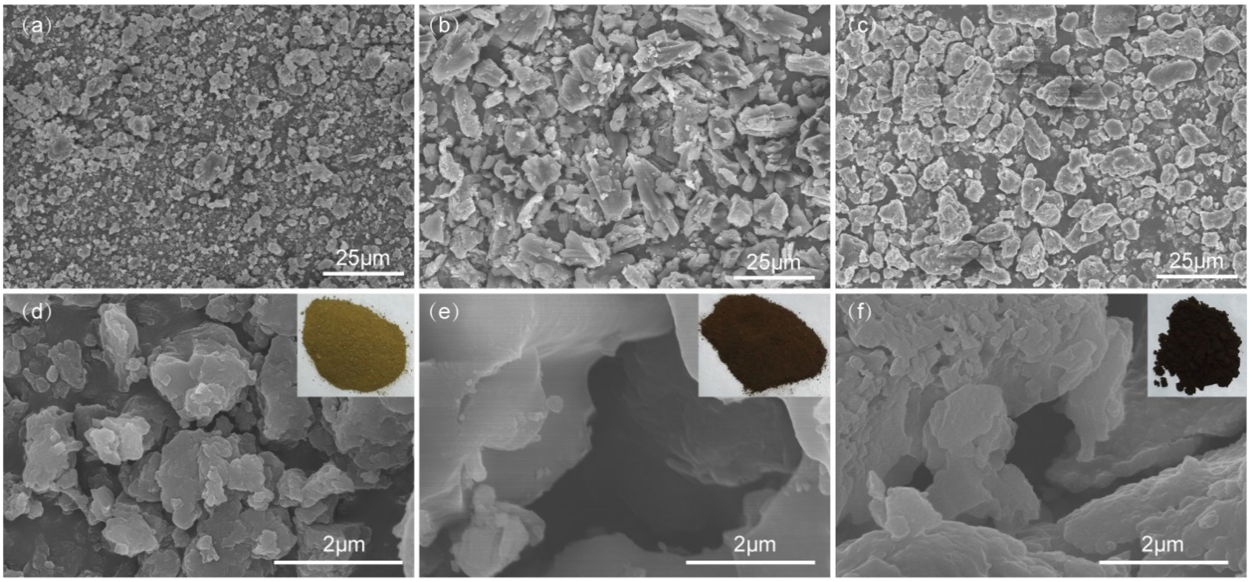

Fig. S1. HRSEM of PBOZ (Cu–MA–BPA) cured in (a, d) glycerol, (b, e) air, (c, f) silicone oil.

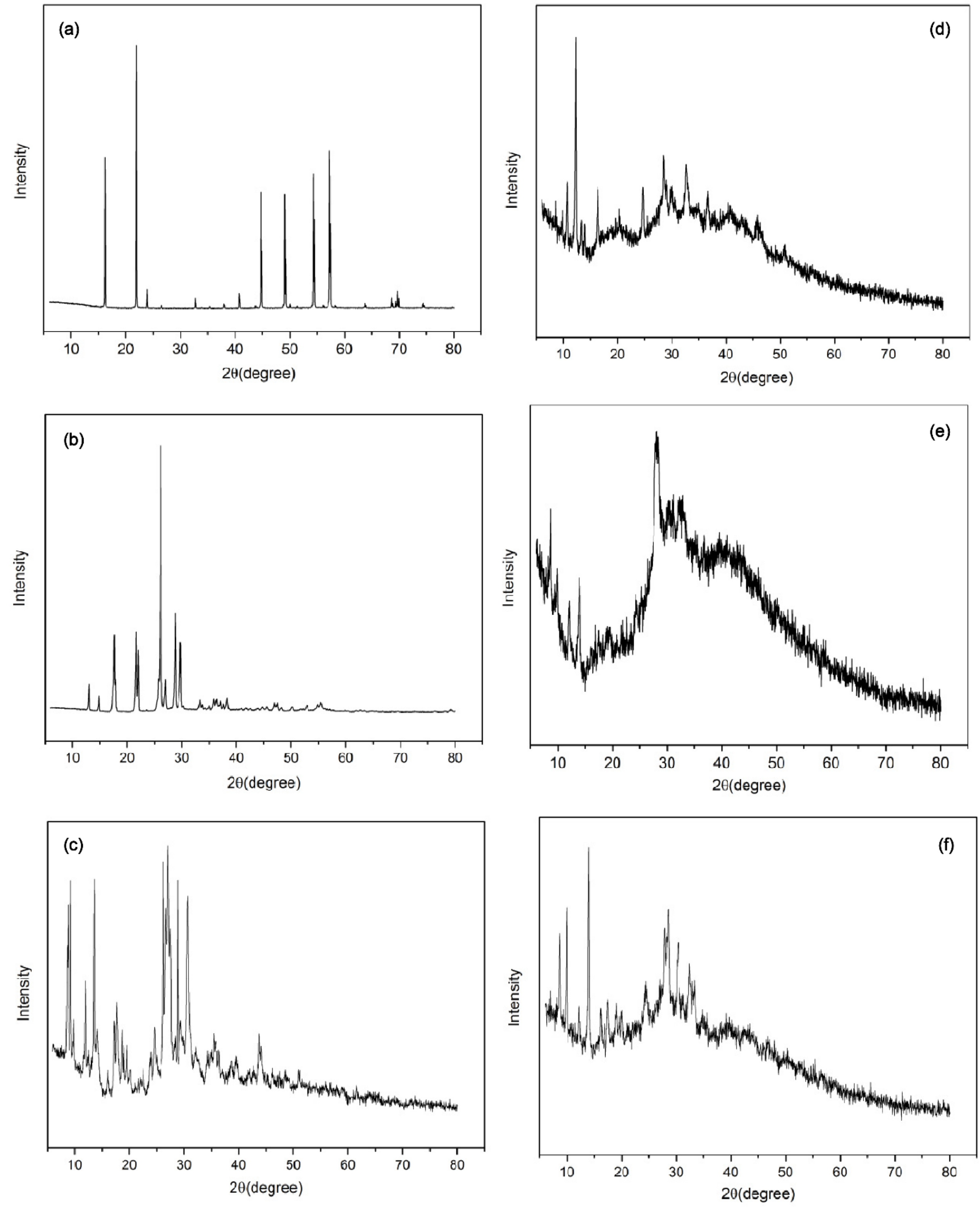

Fig. S2. X-ray diffraction analysis (XRD) of reactants and PBOZ (Cu–MA–BPA). (a) $CuCl_2.2H_2O$, (b) melamine, (c) copper–melamine complex (Cu–MA), (d) PBOZ (Cu–MA–BPA) was cured in glycerol, (e) PBOZ (Cu–MA–BPA) was cured in air, (f) PBOZ (Cu–MA–BPA) was cured in silicone oil.