ORIGINAL ARTICLE

Adsorption of ponceau 4R from aqueous solutions by polyamidoamine–cyclodextrin crosslinked copolymer

Ning Li · Xiao-Mei Lei

Abstract Batch adsorption experiments were carried out for the removal of ponceau 4R (P4R, C.I. 16255) from aqueous solutions using a novel polyamidoamine–cyclodextrin crosslinked copolymer (PAMAM-CD). The influence of several operating variables, such as contact time, initial concentration, pH, ionic strength, was investigated. Results showed that PAMAM-CD exhibited very high adsorption capacity toward P4R. The adsorption capacity of P4R was even up to 254.3 mg/g when the initial concentration of P4R solution was 340 mg/L at 288 K. The maximum adsorption capacity occured at below pH 5. The adsorption rate was fast and over 52% of the equilibrium adsorption value occurred in the first 15 min at 308 K. Adorption kinetics followed the Ho and McKay equation. Intraparticle diffusion was involved in the adsorption process but it is not the only rate-controlling step. Equilibrium isotherm data were precisely fitted by the Langmuir model. The negative values of Gibbs free energy change indicated the spontaneous nature of adsorption. The PAMAM-CD was easily recovered by 2 M HCl as washing solvent and it could be used as a promising alternative adsorbent.

**Keywords** Cyclodextrin · Polyamidoamine · Copolymer · Adsorption · Ponceau 4R

Introduction

Ponceau 4R (P4R, also known as C.I. 16255, cochineal red A, Fig. 1) is a water-soluble azo dye, widely used in food products, drugs, cosmetics, and so on [1]. P4R is classified as a carcinogen in some countries including the United States, Norway and Finland, and is currently listed as a banned substance by U.S. Food and Drug Administration (FDA) [2]. The European Food Safety Authority (EFSA) recently decided to reduce the acceptable daily dose of P4R from 4 mg/kg to 0.7 mg/kg by body mass, due to the health risks entailed by its use [2]. Moreover, like all other dyes, P4R in water bodies can also interfere with the growth of aquatic organisms. Therefore, the wastewater containing P4R must be treated before it is released into the water bodies. Some techniques such as photodecolourization [3], biodegradation [4], oxidative decolorization [5, 6] have been used to remove P4R. However, few reports have shown the removal of P4R by adsorption technique [7]. Adsorption to remove pollutants without disturbing the quality of water or leaving behind any toxic degraded products has competed with electrochemical, biochemical or photochemical degradation techniques [8, 9]. Nowadays polymeric adsorbents are widely employed in the isolation and purification of organic substances, treatment of waste streams, adsorption of organic vapors, and so on [10–12].

β-Cyclodextrin (CD) is cyclic oligosaccharides consisting of 7 glucopyranose units, which are joined together by α(1–4)linkage forming a torus-shaped ring structure (Fig. 2). The ring structure provides a relatively hydrophobic central cavity and a hydrophilic outer surface. The most notable feature of CD is its ability to form inclusion compounds with a very wide range of solid, liquid, and gaseous compounds by molecular complexation [13]. However, CD has to be modified due to its solubility or other reasons. The CD crosslinked with suitable crosslinkers forming insoluble polymers which exhibited specific adsorption ability due to formation of inclusion complex. Cyclodextrin based polymers have been successfully

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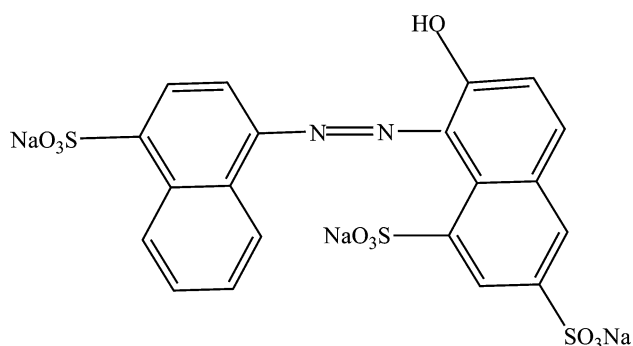
Fig. 1 Chemical structure of ponceau 4R

applied to the removal of diverse substances from water [12, 14–16]. Polyamidoamine (PAMAM, Fig. 2) dendrimers are based on an ethylenediamine core, and branched units constructed from both methyl acrylate and ethylenediamine [17]. The internal nanocavities and facile functionalization of their terminal groups afforded the PAMAM unique characters in a wide range of applications. One of potential applications was their use as efficient water treatment agents for the purification of water but they were very difficult to be separated from water after use [18]. Some studies have shown that incorporation of CDs into PAMAM dendrimers provided unique polymer structures from the combination of two types of molecular cavities, and the polymers possessed simultaneously the partial performance both PAMAM and CD [19]. In previous work, we designed, prepared and characterized a novel insoluble polyamidoamine–cyclodextrin crosslinked copolymer (PAMAM-CD). The copolymer could be used as an adsorbent (one of applications) and it could be easily separated from solvents after use. The preliminary results showed that PAMAM-CD exhibited high adsorption capacities and high removal efficiencies toward both the heavy metal ions and organic compounds in the aqueous solutions [20]. However, the adsorption behaviors, such as influence of adsorption conditions, isotherm and kinetics of adsorption, mechanism of the adsorption, were not discussed. Pursuing our interest in such polymer, we reported the use of PAMAM-CD as adsorbent for the adsorption of dye in water. Due to the fact that the adsorption of P4R on PAMAM-CD has been simply investigated in our previous work [20], this compound was selected as the model dye for this work.

In present paper, the PAMAM-CD copolymer was used to remove P4R from aqueous solutions by batch adsorption. The influence of several operating variables, such as initial concentration, contact time, pH, temperature, was investigated. The isotherms, thermodynamics, kinetics and mechanism of the adsorption were discussed. The one of aims of the present work was to explore the potential of PAMAM-CD copolymer as an adsorbent. This study can provide a valuable example for removal of water-soluble azo dyes from wastewater.
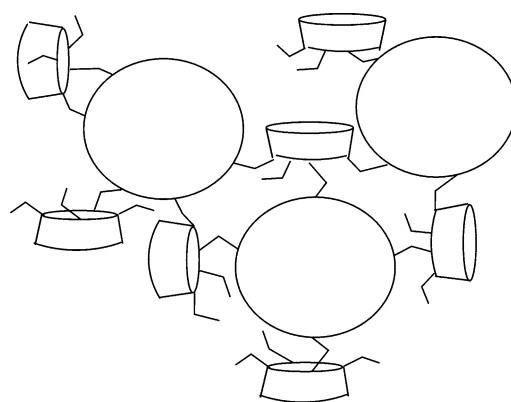
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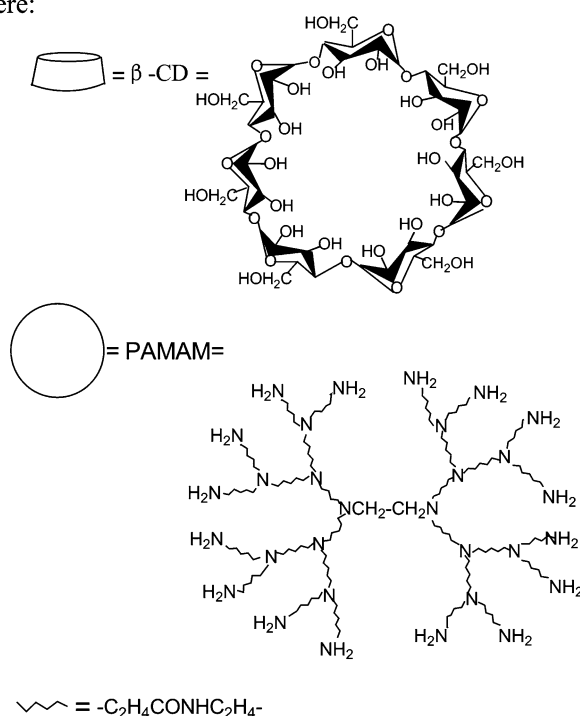
Fig. 2 A possible structure of PAMAM-CD [20]

Materials and methods

Materials

The insoluble crosslinked copolymer containing β-cyclodextrin (CD) structural units and PAMAM (generation 2, G2.0) units has been synthesized (Fig. 2). The synthetic procedure has already been described in detail in our previous work [20]. The product was dried at 110 °C for 1 h, and then crushed and sieved into different particle sizes. Studies were focused on a size fraction of 150–250 μm. The final product (PAMAM-CD) was stored in a desiccator before use. These particles had a hydrogel nature with a high capacity for absorbing water. The density of the swollen polymer gel was higher than that of water. The

Brunauer–Emmet–Teller (BET) surface area (m^2/g) and BET average pore diameter (nm) in the dry state were determined by the BET method from low-temperature nitrogen adsorption isotherms at 77 K using a Micromeritics ASAP-2020 analyzer. The surface area was 1.19 m^2/g. The results of elemental analysis (with a Vario MICRO Elemental Analyzer, Germany) were concluded that two cyclodextrin molecules were cross-linked with one PAMAM (G2.0) molecule [20].

The P4R was commercial product and used without purification. The other chemicals were of analytical grade. All aqueous solutions were prepared with deionized water that had been passed through a Millipore Milli-Q Plus water purification system. An accurate quantity of the adsorbate was dissolved in water to prepare a stock solution (the solution was stable in studied range of time) and the solutions for adsorption tests were prepared from the stock solution to the desired concentrations by successive dilutions. A calibration curve was first prepared for P4R in order to calculate the concentration of each test.

Adsorption experiments

Experimental data were determined by the following batch method: in each experiment, 50 mg of dry PAMAM-CD was mixed with 50 mL aqueous solution containing a known concentration P4R in a sealed flask. The flask was shaken with a shaker at 60 rpm under dark condition. The adsorption temperatures and the concentrations of P4R varied according to experiments. The adsorbent was removed by centrifugation before measurement. The residual adsorbate concentration in solution was determined at the wavelength of maximum absorption (508 ± 2 nm) using a 722 visible spectrophotometers (Shanghai, China). Each experiment was done three times under identical conditions. These data were used to calculate the adsorption capacity of the adsorbent by Eq. 1:

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

where, q_e is the amount of adsorbate adsorbed at equilibrium (mg/g); C_0 is the initial adsorbate concentration in liquid phase (mg/L); C_e is the liquid phase adsorbate concentration at equilibrium (mg/L); V is the volume of adsorbate solution used (L); and m is the mass of adsorbent used (g).

Effect of contact time

Dry PAMAM-CD samples were placed separately in a series of flasks containing 280 mg/L P4R solutions at pH 5. The contents of these flasks were agitated at 283, 298 and 308 K, respectively. At different time intervals, the remaining concentration of the adsorbate in different solutions was determined.

Equilibrium studies

The equilibrium studies were conducted by the following method: in each experiment, 50 mg of dry PAMAM-CD was mixed with P4R solution at a known different initial concentration (from 130 to 350 mg/L) at pH 5 in a sealed flask. The contents of the flask were swayed for 12 h at set temperature. Then the remaining concentration of the adsorbate was determined. The experiments were done at 288, 293, 298, 303 and 308 K, respectively.

Effect of pH

To evaluate the effect of the pH on the adsorption of P4R, tests were carried out in solutions at 298 K. Dry PAMAM-CD samples (each 50 mg) were placed separately in a series of flasks containing 25 mL of 560 mg/L P4R solutions. The desired pH was adjusted with 1 M HCl or 1 M NaOH. Then the solutions were diluted to 50 mL with water to obtain 280 mg/L P4R solutions. The contents of these flasks were swayed on a shaker for 12 h. Then the remaining concentration of P4R was determined and adsorption capacity was calculated by Eq. 1. The experiments were conducted at different pH from 2 to 7.

Effect of salt

The effect of NaCl on the adsorption of the P4R was investigated at 298 K. 50 mg of PAMAM-CD samples were placed in series of flasks containing 50 mL of P4R solutions (initial concentration: 280 mg/L) and different NaCl concentrations (0–300 mg/L). The contents of these flasks were agitated for 12 h. Then the remaining concentration of the adsorbate was determined.

Interactions between PAMAM and P4R

The molar ratio method [21] was utilized to observe the interactions between PAMAM and P4R and determine the stoichiometric ratio of PAMAM-P4R complexes through spectrophotometer measurements. The concentration of P4R was kept constant (0.0225 mM, pH 4) but varying the molar concentration of PAMAM. The mixture solutions were stable for 12 h at 290 K before measurements.

Desorption

To recover the adsorbed adsorbate and reuse the adsorbent, 0.3 g PAMAM-CD, with previously adsorbed equilibrium adsorbate, was shaken for 0.5 h at 318 K with 20 mL 2 M

HCl as washing solvent each time. Then, the adsorbent was separated by centrifugation and the supernatants were determined by spectrophotometers. Each experiment was done three times under identical conditions. The recovery ratio was defined as the ratio of the adsorbate amount in HCl solution to the amount previously adsorbed on PA-MAM-CD.

## Results and discussion

Effect of contact time

In order to ascertain the minimum time to reach adsorption equilibrium, a study on the effect of contact time will be necessary. Fig. 3 shows the effect of contact time on P4R adsorption. It was shown that adsorption increased instantly at initial stages due to rapid attachment of P4R to the surface of the polymer. Over 35% of the equilibrium value occurred in the first 15 min at 288 and 298 K, however, even 52% of the equilibrium value occurred in the first 15 min at 308 K. The results were also confirmed by the following initial adsorption rate and half-adsorption time analysis. At about 90 min, over 80% of the equilibrium value reached at all temperatures. And thereafter the rate of adsorption was found to be slow because the P4R molecules had to diffuse into the interior of adsorbent with the gel particles of PAMAM-CD gradually swelling in the solution, until the equilibrium reached and remained constant at nearly 240 min contact time. In fact, if the adsorbent is allowed to swell in water prior to the adsorption experiments, the equilibrium time is shorter. The fast adsorption rate was beneficial to the practical application of the PAMAM-CD polymer as adsorbent. However, for subsequent experiments, the samples were shaken for 12 h to ensure the adsorption equilibrium.

Adsorption kinetics

Adsorption kinetics parameters, such as the adsorption rate constant of the kinetics, the initial adsorption rate, as well as half-adsorption time, which can control the residence time of the adsorbate uptake at the solution-solid interface and provide valuable insights into water treatment process design, are of great importance for the application of adsorbents.

In order to monitor the kinetics of the adsorption of P4R on PAMAM-CD, a pseudo 2nd order rate equation was applied. The pseudo 2nd order model proposed by Ho and McKay could be represented in the following linear form [22]:

$$\frac{t}{q_t} = \frac{t}{q_e} + \frac{1}{k_2 q_e^2} \tag{2}$$
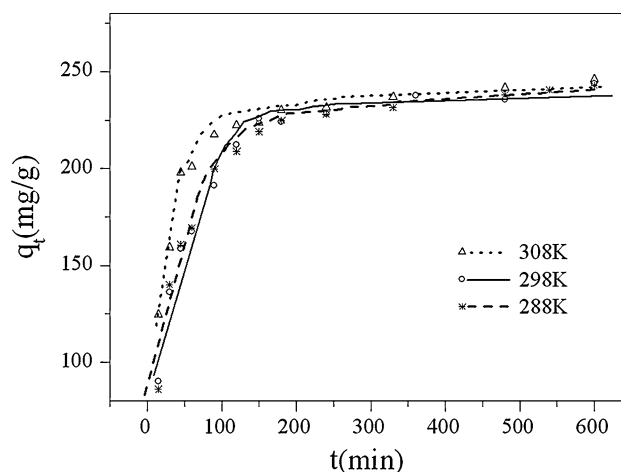
Fig. 3 Effect of contact time on P4R adsorption (conditions: adsorbent: 50 mg; initial concentration: 280 mg/L; volume: 50 mL)

where, q_t and q_e are the amount adsorbed at time t and at equilibrium (mg/g), respectively; k_2 is the rate constant (g mg^{-1} min^{-1}). The values of k_2 and q_e were calculated from the intercept and slope of the linear plots of t/q_t against t. This model is based on the assumption that the adsorption follows a chemisorption process [22]. The results (with coefficients of determination over 0.99, Table 1) revealed that the ongoing adsorption process occured via pseudo 2nd order kinetics for PAMAM-CD at different temperatures. At the same time, the calculated $q_{e,cal}$ values from the model were also close to the experimental $q_{e,exp}$ values, which also sustained the above mentioned deduction.

The initial adsorption rate (u, mg g^{-1} min^{-1}) and half-adsorption time ($t_{1/2}$, min) of PAMAM-CD for P4R were estimated in Table 1 according to the following equations [23]:

$$u = k_2 q_e^2 \tag{3}$$

$$t_{1/2} = (k_2 q_e)^{-1} \tag{4}$$

Half-adsorption time, which is defined as the time required for the adsorption to take up half as much P4R as its equilibrium value, is an effective measurement of adsorption rate. As is shown in Table 1, initial adsorption rate of PAMAM-CD for P4R increased with the increase of the temperature, and the half-adsorption time was shorter at higher temperature, due to the diffusion rate of P4R molecules becoming more rapid with the increase of the temperature.

Rate-controlling step in the process of adsorption

In general, adsorption process consists of four consecutive steps: bulk solution transport, film diffusion, intraparticle diffusion, and adsorption on the surface or pores [24]. One

Table 1 Ho and McKay adsorption kinetics parameters of PAMAM-CD for P4R

| Temperature (K)	$q_{e,exp}$ (mg g^{-1})	$q_{e,cal}$ (mg g^{-1})	k_2 (g mg^{-1} min^{-1})	R^2	$t_{1/2}$ (min)	u (mg g^{-1} min^{-1})
288	244.56	251.89	1.48×10^{-4}	0.9995	26.79	9.40
298	243.65	250.63	1.50×10^{-4}	0.9995	26.66	10.29
308	247.16	248.76	2.63×10^{-4}	0.9991	15.28	17.19

or more of these steps can control the adsorption rate altogether or individually. The lowest step limits the overall adsorption rate. In a well-agitated batch system, the external diffusion resistance is much reduced. The last step, adsorption, is usually very rapid in comparison to the first three steps. According to the literature, film diffusion and diffusion into particle pores (intraparticle diffusion) often control an adsorption process. In order to investigate the step possibly controlling the adsorption of P4R adsorption onto PAMAM-CD under the selected conditions, the experimental data were fitted with the Weber–Morriss equation, which is the most commonly tested model [24, 25]:

$$q_t = k_i t^{0.5} + c \qquad (5)$$

where, q_t (mg/g) is the amount of the adsorbed at time t (min), k_i (mg g^{-1} min$^{-1/2}$) is the intraparticle diffusion rate constant, and c is the intercept (mg/g). If the value of c is zero, then the rate of adsorption is the sole rate controlled by intraparticle diffusion for the entire adsorption period. However, the plot of q against $t^{0.5}$ usually shows more than one linear portion. If the plot does not pass through the origin, this is indicative of some degree of boundary layer control and the intraparticle diffusion is not the only rate-controlling step, but also other processes may control the rate of adsorption [14]. As seen from Fig. 4, the plots were not linear over the whole time range, implying that more than one process affected the adsorption [26]. In general, the three plots at different temperatures had the same features and there were two different portions: the first straight portion was due to the boundary layer effect and the second linear portion due to intraparticle or pore diffusion. The similar dual or multiple linear plots were also reported in the literature [14, 26–28]. It can be also observed that the plots did not pass through the origin, indicating that intraparticle diffusion was involved in the adsorption process but it was not the only rate-controlling step and some other steps also played an important role [14].

Effect of the initial concentration

The effect of various initial P4R concentrations on adsorption was recorded in Fig. 5. The results showed that adsorption capacities of PAMAM-CD for P4R increased
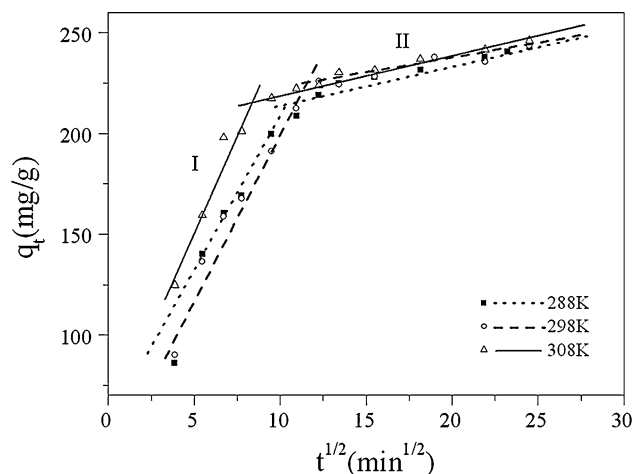

Fig. 4 Plots of q_t versus $t^{0.5}$ for the adsorption of P4R by PAMAM-CD at different temperatures (conditions: adsorbent: 50 mg; initial concentration: 280 mg/L; volume: 50 mL)

almost linearly with the increase of the initial concentration. The adsorption capacity of PAMAM-CD was 135 mg/g when the initial concentration of P4R solution was 136 mg/L at 288 K, while it was even up to 254.3 mg/g when the initial concentration of P4R solution was 340 mg/L at the same temperature. Similar results were observed at other temperatures. As can be also seen from Fig. 5, adsorption of P4R on PAMAM-CD was not significantly affected by temperature within the studied range. From the trend of adsorption capacity with respect to concentrations as shown in Fig. 5, the adsorption almost reached saturation at about 350 mg/L of initial P4R concentration, indicating that the adsorption of P4R on PAMAM-CD was monolayer. These would be proved by the following Langmuir isotherm analysis.

Adsorption isotherms

Adsorption isotherms describe how adsorbates interact with adsorbents and so, are critical in optimizing the use of adsorbents. In order to optimize the adsorption systems for the removal of P4R from solutions, it is important to investigate the equilibrium properties of adsorption process. Four isotherm equations, commonly used in the literature, were applied to the present study. These models are Temkin [29], Dubinin–Radushkevich [30], Freundlich [31] and Langmuir [32]. The goodness-of-fit for isotherm
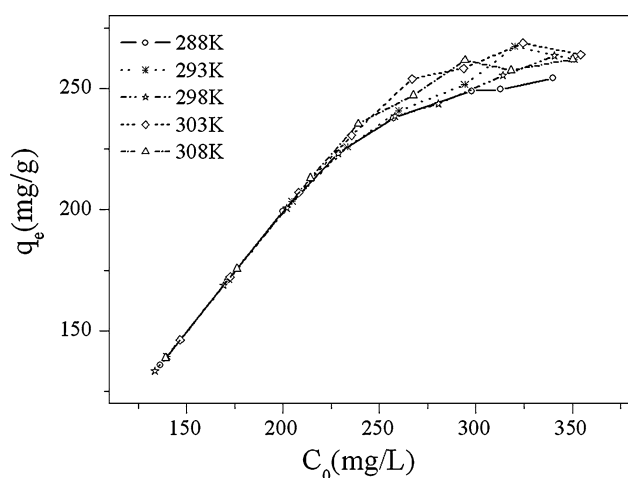
Fig. 5 Effect of initial concentration on adsorption (conditions: adsorbent: 50 mg; volume: 50 mL)

equations was estimated by the coefficient of determination (R^2). However, the coefficients of determination of all models were low except Langmuir model. The Langmuir model is the most commonly used for monolayer adsorption of adsorbate on the surface of adsorbent. The model is based on several assumptions [14, 32, 33]: (a) the adsorption takes place at specific homogenous sites; (b) all sites are identical and energetically equivalent, and there are no interactions between molecules adsorbed on neighboring sites (adsorption energy does not depend on the degree of occupation of the active sites) (c) once an adsorbate molecule occupies a site, no further adsorption can take place at that site (monolayer adsorption); (d) the adsorbent has a finite capacity for the adsorbate. The linear Langmuir equation was given below:

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \frac{C_e}{q_m} \tag{6}$$

where, C_e (mg/L) is the equilibrium P4R concentration in solution, q_e (mg/g) is adsorption capacity at equilibrium, b is the Langmuir constants, q_m (mg/g) is the maximum adsorption capacity and represents a practical limiting adsorption capacity when the adsorbent surface is fully covered with monolayer adsorbate molecules. The validity of model can be checked from the coefficient of determination (R^2). The Langmuir isotherm parameters for the

adsorption of P4R onto PAMAM-CD are presented in Table 2.

Apparently, the R^2 values showed that experimental data were well described by the Langmuir isotherm model. On the basis of the Langmuir analysis, the maximum adsorption capacities were determined to be 251.2, 264.5, 261.8, 266.8 and 262.1 mg of P4R per gram of PAMAM-CD at 288, 293, 298, 303 and 308 K, respectively. These values demonstrated that PAMAM-CD exhibited very high adsorption capacity toward P4R. In general, temperature had complicated effects for the adsorption: it changed the chemical potential of PAMAM-CD and the degree of dissociation of the P4R, affected the adsorption and desorption equilibrium, and so on. On the whole, there was no significant change in the adsorption capacity with altering temperature under our experimental conditions. Compared with some data in the literature [7, 33, 34], the results also revealed the potential of the polymer to be an effective adsorbent for removing azo dyes.

Further, the essential characteristic of the Langmuir isotherm can be described by a dimensionless constant, namely separation factor (R_L), which is defined by the following equation [35]:

$$R_L = (1 + bC_0)^{-1} \tag{7}$$

where, C_0 is the initial concentration (mg/L) and b is the Langmuir constant. R_L is related to the nature of adsorbent/adsorbate interaction and isotherms type: unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$) [35]. The calculated R_L values at different initial P4R concentration are reported in Fig. 6. In all investigated range, R_L values have been found less than unity, indicating that adsorption process of PAMAM-CD for P4R was favorable. These results were consistent with the following Gibbs free energy change (ΔG_i) analysis. Also higher R_L values at lower P4R concentrations showed that adsorption was more favorable at higher initial concentration of P4R.

Thermodynamic parameters

The ΔG_i was calculated to evaluate the thermodynamic feasibility of the process. The Langmuir constant 'b' can be used for estimation of the said thermodynamic parameters using following equation [36]:

Table 2 Langmuir isotherm parameters for adsorption P4R by PAMAM-CD

Parameters	Temperature (K)				
	288	293	298	303	308
q_m (mg/g)	251.2	264.5	261.8	266.8	262.1
b (L/mg)	1.50	1.13	1.03	2.34	2.12
R^2	0.9992	0.9992	0.9988	0.9995	0.9998
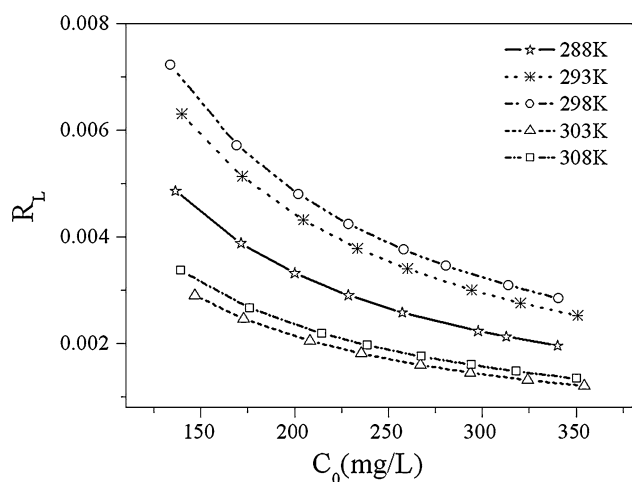
Fig. 6 Separation factors for P4R on PAMAM-CD at different temperatures
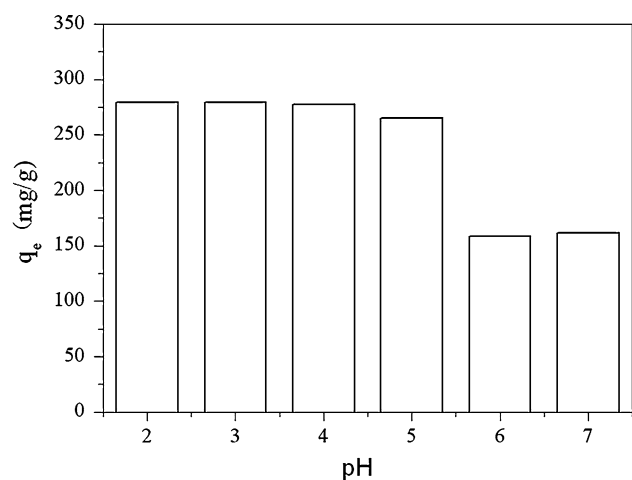
Fig. 7 Effect of initial pH on adsorption of P4R

$$\Delta G_i = -RT \ln b_i \qquad (8)$$

where b_i is the Langmuir constant (L/mol), R is the gas constant and T is temperature in Kelvin. The calculated ΔG_i values were found to be −32.85, −32.72, −33.05, −35.68 and −36.02 kJ/mol at 288, 293, 298, 303 and

308 K, respectively. The negative ΔG_i values indicated the feasibility and spontaneous nature of the adsorption process. These results were consistent with the foregoing separation factor analysis. The change in entropy (ΔS) and change in enthalpy (ΔH) were not reported because the errors involved in their calculations were very large when adsorption of P4R on PAMAM-CD was not significantly affected by temperature.

Effect of pH

The effect of pH on the adsorption of P4R on PAMAM-CD is shown in Fig. 7. From Fig. 7, it was observed that the adsorption was pH-dependent. The maximum adsorption capacities occurred at initial pH <5. The amount of P4R adsorbed was found to show a decline at higher initial pH. The result can be attributed to the adsorption mechanism. The adsorption process was probably simultaneously dominated by weak Van Der Waals force, hydrogen bonding, inclusion, dimerization, electrostatic attraction, etc.

The groups (–NH$_2$, –NH– and –OH) of the PAMAM-CD can form hydrogen bond with the groups (–OH and –N=N–) of P4R. In addition, it is well known that CD molecules have a capacity to form inclusion complexes, and the PAMAM-CD polymer retain the inclusion property of CD molecules. Some research has proved the P4R could form inclusion complexes with CD [37]. We used the β-cyclodextrin-epichlorohydrin polymer (CDP, the typical characteristics were reported in previous work [15]) as adsorbent to remove P4R from aqueous solutions at same conditions, and found the adsorption capacity of CDP was 20.5 mg/g, which further confirmed that P4R could form partial inclusion complexes with CD. It is well known that ionic dyes tend to aggregate in diluted solutions, leading to dimer formation, and sometimes even higher order aggregates [38]. P4R molecules probably also formed some dimmer and gathered on the surface of PAMAM-CD. P4R adsorption also partly occurred through electrostatic attraction on protonated amine groups. Scheme 1 briefly describes the adsorption mechanism: in the presence of H$^+$,

Scheme 1 Mechanism of P4R adsorption by PAMAM-CD under acidic conditions
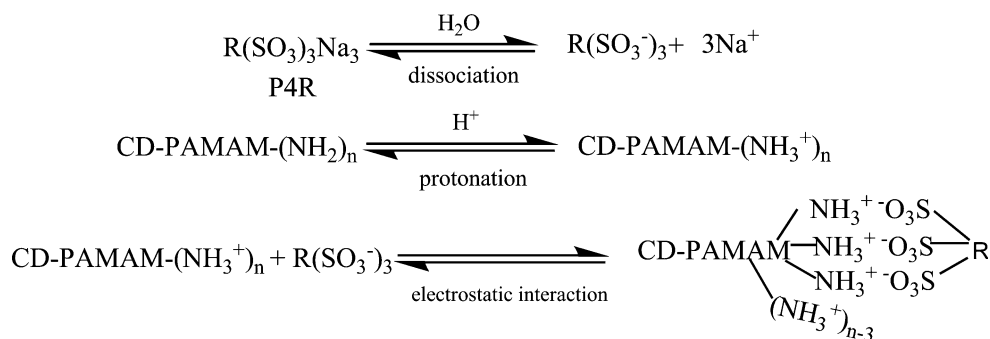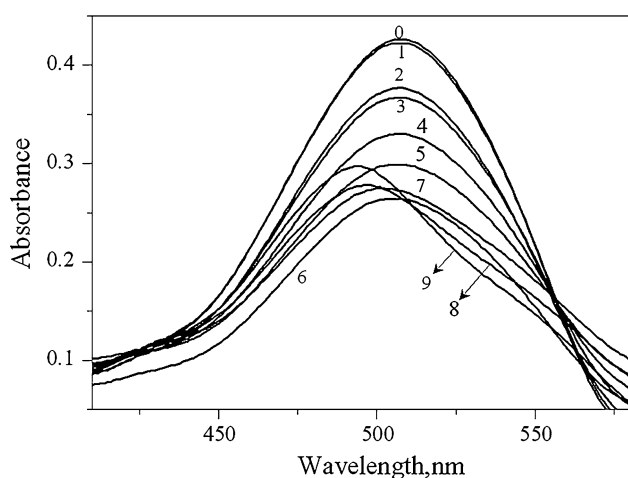
Fig. 8 Visible absorption spectra of P4R (0.0225 mM) with increasing PAMAM concentration at 290 K: (*0*) Without PAMAM; (*1*) 1.69×10^{-4} mM; (*2*) 3.37×10^{-4} mM; (*3*) 5.06×10^{-4} mM; (*4*) 8.42×10^{-4} mM; (*5*) 1.18×10^{-3} mM; (*6*) 1.52×10^{-3} mM; (*7*) 2.02×10^{-3} mM; (*8*) 2.36×10^{-3} mM; and (*9*) 2.95×10^{-3} mM
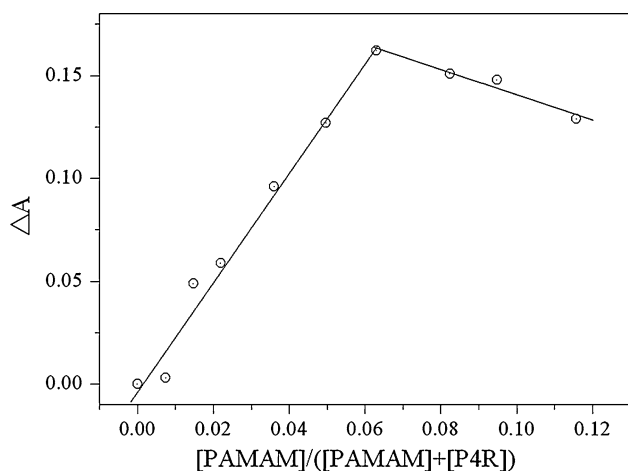
Fig. 9 Elucidation of the stoichiometric ratio of PAMAM-P4R complexes

the amino groups of PAMAM-CD became protonated; also, in aqueous solution, the P4R ($R(SO_3)_3Na_3$) was first dissolved and the sulfonate groups of P4R were dissociated and then P4R were converted to anionic dye ions; so the adsorption process proceeded due to the electrostatic attraction between these two counterions. Chatterjee et al. [39] also found that the adsorption of anionic dye (eosin Y) on chitosan-grafted materials had similar mechanism.

The adsorption capacities decreased rapidly at pH >5, which was probably due to the change of electrostatic attraction. In general, increasing pH of solution probably had two main effects in the adsorption process. On the one hand, it was in favor of adsorption (electrostatic attraction) due to the increase of dissociation of –OH groups of the P4R ($pK_a = 6.8$). On the other hand, fewer protons could

be available to protonate the amine groups of PAMAM-CD and the number of positively charged (available sites) decreased; furthermore, the more dissociated P4R molecules were more unfavorable to inclusion complexation with cyclodextrin due to a negative effect on the driving forces of inclusion complexation [16], all these resulted in decreasing adsorption of PAMAM-CD to P4R. The final result was that the adsorption capacities of P4R decreased with increase of pH.

In particular, pH was also known to affect the structural stability of P4R, and therefore its color intensity. It was found that the color intensity of P4R in aqueous solution was stable at $2 < pH < 7$ at least 120 h under dark condition and the same P4R concentration had the same color intensity at different pH ($2 < pH < 7$). However, color intensity was different with the change of pH (pH >7) at the same P4R concentration, due to the ionization of the hydroxyl groups of P4R. Therefore the studies on the effect of pH were performed within pH 7. Due to the facts that the adsorption capacity of P4R on PAMAM-CD at pH 5 was slightly lower than that of at below pH 5 (maximum relative error being 4.3% only) and some extra strange ions could be avoided in the adsorption systems, all the other adsorption tests in the work were performed at natural pH values of P4R solutions (pH 5). The pH of solution was only slightly changed before and after adsorption.

In order to further evaluate the complex ability between PAMAM and P4R, the stoichiometric ratio of complexes was tested by molar ratio method [21]. Figures 8 shows the visible absorption spectra of P4R were remarkably altered and the maximum absorption peak of P4R gradually shifted from 506 to 495 nm by increasing PAMAM concentration. These data might suggest the possibility of interactions between PAMAM and P4R.

Plotting the differences between the measured absorbance values versus mole fraction reveals molar ratio at which complexation takes place from the point of inflection of the produced curve. Figure 9 shows a change in slope at PAMAM mole fraction of 0.063, indicating formation of 14.8:1(average) P4R: PAMAM complex.

All the results showed that there were obvious interactions between the P4R and two different structural units (i.e., CD units and PAMAM units) of PAMAM-CD copolymer. Furthermore, there were different interaction mechanisms for CD and for PAMAM in adsorption process, so the PAMAM-CD copolymer possessed simultaneously the partial performance both PAMAM and CD and could adsorb more various adsorbates.

Effect of salt

The effect of the interfering ion on the adsorption of P4R was evaluated. The result showed that there was only

slightly decreased in the adsorption capacity with increasing ionic strength of the solutions under our experimental conditions (Figure not shown). The adsorption capacity of PAMAM-CD for P4R was 243.7 mg/g when the initial concentration of NaCl solution was 0 mg/L at 298 K, and it was 242.1, 237.9 and 236.7 mg/g when the initial concentration of NaCl solution was 100, 200 and 300 mg/L at the same temperature, respectively. In general, NaCl probably had two main functions in the adsorption process. On the one hand, it probably screened the electrostatic interactions of opposite charges in PAMAM-CD and P4R molecules and resulted in a decrease of the amount adsorbed with increasing salt concentrations. On the other hand, it enhanced the degree of dissociation of the P4R and involved an increase of the amount adsorbed. On the whole, the adsorption capacity decreased.

Desorption

One of the important goals in development of adsorbent is its regeneration capacity. On the one hand, regeneration can allow the repeated use of adsorbent. On the other hand, isolation of adsorbate can allow its reuse or efficient disposal. The average recovery ratios of P4R were $62.2 \pm 4.8\%$ and $23.4 \pm 3.5\%$ at the first and second time washing, respectively. And the value is up to $96.8 \pm 2.2\%$ after washing 4 times. There was not obvious change in the adsorption capacity after this treatment. The regenerated PAMAM-CD could adsorb more than 90% P4R in contrast to the first adsorption capacity. Even after 5 times regeneration tests were performed, the regenerated PAMAM-CD could adsorb $90 \pm 5\%$ adsorbate in contrast to the first sorption capacity.

This showed the stability and recyclable values of the PAMAM-CD. In fact, the higher concentration HCl was used as washing solvent (such 4 M HCl), the recovery ratio (especially the first time) was higher and the regeneration effect became better.

Conclusions

Results of batch adsorption experiments showed that polyamidoamine–cyclodextrin crosslinked copolymer (PAMAM-CD) exhibited high adsorption capacity and acceptable adsorption time toward anion azo dyes like ponceau 4R (P4R). Adsorption kinetics followed the Ho and McKay model for P4R on PAMAM-CD. Equilibrium isotherm data were satisfactorily fitted by the Langmuir equation. On the basis of the Langmuir analysis, the maximum adsorption capacities were determined to be 251.2, 264.5, 261.8, 266.8 and 262.1 mg of P4R per gram of PAMAM-CD at 288, 293, 298, 303 and 308 K, respectively. The adsorption of P4R on PAMAM-CD was spontaneous. The PAMAM-CD was easily recovered by

concentrated HCl as washing solvent. The PAMAM-CD copolymer can provide one of possibilities for applications in water treatments. In order to verify whether the observed behavior is generally accepted, some additional work is in progress in subsequent studies.

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