Brilliant red X-3B uptake by a novel polycyclodextrin-modified magnetic cationic hydrogel: Performance, kinetics and mechanism

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ABSTRACT

A novel polycyclodextrin-modified magnetic cationic hydrogel (PCD-MCH) was developed and its performance, kinetics and mechanism for the removal of reactive brilliant red X-3B (X-3B) were studied. The results showed that the zeta-potential of PCD-MCH was 32.8 to 16.7 mV at pH 3.0–10.5. The maximum X-3B adsorption capacity of PCD-MCH was 2792.3 mg/g. The adsorption kinetics could be well-described by the Weber–Morris model and the homogeneous surface diffusion model (HSDM). Diffusion stages corresponding to surface or film diffusion, intra-particle or wide mesopore diffusion, and narrow mesopore/micropore diffusion occurred at 0–120, 120–480 and 480–1200 min, respectively. The latter two diffusion stages were rate-controlling for X-3B adsorption kinetics. At the initial X-3B concentration of 600 mg/L, the diffusion coefficient ($D_s$) and external mass transfer coefficient in the liquid phase ($k_F$) were $3 \times 10^{-11}$ cm$^2$/min and $4.68 \times 10^{-6}$ cm/min, respectively. X-3B approaching the center of PCD-MCH particles could be observed at 360 min. At the end of the third diffusion stage, the $C_p$ at $q/q_e = 0$ was 45.20 mg/L, which was close to the homogeneous $C_p$ value of 46 mg/L along the radius of PCD-MCH particles. At pH 3.0–10.0, PCD-MCH showed stable X-3B adsorption capacities. After five regeneration-reuse cycles, the residual adsorption capacity of regenerated PCD-MCH was higher than 892.7 mg/g. The corresponding adsorption mechanism was identified as involving electrostatic interactions, cyclodextrin cavities and hydrogen bonds, of which cyclodextrin cavities showed prominent capture performance towards dye molecules through the formation of inclusion complexes.

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Introduction

It is well known that dye wastewater is a major problem in environmental protection and wastewater treatment. Each year over 280,000 tons of dyes are used in industry (Jin et al., 2007), of which azo dyes are toxic and also potentially carcinogenic, due to their azo groups (N=N→), aromatic rings and sulfonate group. Usually, anaerobic–aerobic biological treatment is used to degrade dyes in wastewater. However, the treatment efficiencies of these biological technologies do not meet the effluent standard requirements due to the difficult biodegradability of many synthetic dyes (Dong and Wang, 2016b; Guieysse and Norvill, 2014; Solis et al., 2012). Therefore, many physicochemical techniques have been used as pre-, inter-, or post-treatment strategies to improve the dye removal rate (Shoreshi and Haghighi, 2003; Solis et al., 2012). Among the above technologies, adsorption is a simple, cost-effective and high-performance means of dye removal (Xiao et al., 2015).

In studies of azo dye adsorption, Reactive Brilliant Red X-3B (X-3B) has often been used as a model azo dye for treatment. Several types of adsorbents have been developed for X-3B removal from wastewater, while their maximum adsorption capacity for X-3B was only 1434.5 mg/g at the initial X-3B concentration of 100–1500 mg/L (Li et al., 2017; Wang et al., 2014; Xiao et al., 2015). Moreover, the adsorption capacities of most of adsorbents are pH-dependent. For instance, the adsorption capacities of LDHs-3 (Anbia et al., 2010), TG (Maria Rahman et al., 2014), MFe3O4/CSNPs (Cao et al., 2014), NH4+–MCM-41 (Qin et al., 2009), and Ti–CSMIP (Deng et al., 2017) towards X-3B decreased with the increase of pH value. In the report of Wu et al. (2007), their organic and carbon aerogels maintained very low X-3B adsorption capacities within the pH range 4–12. Therefore, for X-3B adsorption, it is still necessary to develop a novel absorbent with high adsorption capacity and pH stability.

Recently, a type of magnetic cationic hydrogel (MCH) and its modified composite were developed for anionic pollutant adsorption. The MCH developed by Lo’s research group (Lo et al., 2011; Rao et al., 2011) showed a high zeta potential (ZP) of 48–30 mV at pH 3–12, and exhibited good performance in the liquid phase (HA) adsorption. In the studies of Dong et al., a series of MCH modified composites, such as MGO–CH (Dong and Wang, 2016b), MCH-La (Dong and Wang, 2016a), and La3+(ion)/La(OH)3-W/La(OH)3-EW-loaded-MCH (Dong et al., 2017), presented excellent removal efficiencies towards AR88, F–, and PO4 3–, respectively. In particular, the adsorption capacity of AR88 on MGO-CH could reach 3476.7 mg/g. In the above studies, the numerous cationic adsorption capacity of AR88 on MGO-CH could reach a significant increase of pH value. In the report of Wu et al. (2007), their anionic dye X-3B uptake.

In addition, several research studies indicated that β-Cyclodextrin (β-CD) showed good performance in dye adsorption. Towards C.I. Basic Blue 9 (BB9) removal, Crini and Peindy (2006) developed CD/CMC adsorbents (cyclodextrin-based material) with the monolayer adsorption capacity of 54.5 mg/g. They identified that the aforementioned adsorption was dependent on the presence of carboxylic groups. An environmentally friendly dual-function adsorbent of EDTA-crosslinked β-CD was reported by Zhao et al. (2015) to simultaneously remove metals and cationic dyes. The β-CD in EDTA-β-CD could capture Methylene Blue molecules through the formation of inclusion complexes (Zhao et al., 2015). Moreover, Alsbaiee et al. (2016) fabricated a porous β-CD polymer with rigid aromatic groups, high-surface-area and mesoporous structure. At environmentally relevant concentrations of organic micropollutants, this polymer demonstrated more rapid removal of their complex mixture than a leading activated carbon. In these studies, the torus-shaped ring structure of β-CD with internal hydrophobic and external hydrophilic properties provided a cavity for organic species inclusion through host–guest interactions, especially aromatic molecules and other small organic ones owing to their suitable size and polarity (Mura, 2014; Zhao et al., 2009). In X-3B molecules, the benzene ring structure presented a hydrophobic backbone and a size of 0.5 nm, which could adapt to inclusion capture by β-CD.

Due to their different mechanisms of anion adsorption, the MCH and β-CD structures can be coupled into a hybridized composite and play a multifunctional role in the removal of these anions. Thus, in this study, a magnetic cationic hydrogel modified by polycyclodextrin (PCD-MCH) was developed for X-3B adsorption, which was focused on the following objective: (1) PCD-MCH was characterized by Zeta potential, VSM, ATR-IR, SEM, and TEM; (2) The adsorption isotherms and kinetic curves were provided and fitted by the corresponding models to determine the adsorption capacity and rate constant, the diffusion coefficient (Dk) and external mass transfer coefficient in the liquid phase (kL), respectively. (3) The effects of solution pH and co-existing anions on adsorption efficiency were systematically studied, as well as the recycling of the spent PCD-MCH. (4) The adsorption mechanism of X-3B on PCD-MCH was identified by ATR-IR, XPS and other related experimental results.

1. Materials and methods

1.1. Materials

Analytical grade (3-acrylamidopropyl) trimethylammonium chloride (APTMACl; 75 wt.% in water), N,N′-methylenebis (acrylamide) (MBA), and N,N,N′,N″-tetramethylmethylenediamine (TEMED) were purchased from Sigma–Aldrich (Beijing China) and used without further purification. Potassium persulfate (KPS), tetrafluoroterephhalonitrile, tetrahydrofuran (THF), K2CO3, Fe3O4 nanoparticles and β-CD of chemical purity were obtained from Sinopharm Chemical Reagent Co., Ltd. (China). THF was purified and dried in an activated alumina solvent purification column. The D50 of the black Fe3O4 powder was 20 nm. The azo dye X-3B (C19H10Cl2N6Na2O7S2) was...
the adsorbate and was purchased from Shanghai Macklin Biochemical Co., Ltd.; its physicochemical characteristics are presented in Appendix A Table S1.

### 1.2. Preparation of PCD-MCH

PCD was synthesized using a previously described method (Alsaleh et al., 2016). A flame-dried 250 mL conical flask equipped with a magnetic stir bar was stirred with 10 g of PCD, 25 mL of APTMACl with addition of 0.8 mL of deionized water. After all MBA was dissolved, 20 mL of TEMED, 0.3 g Fe3O4 and 0.5 g of PCD was added into the matrix. When the matrix was homogeneously mixed, 0.6 mL of saturated KPS solution was added. The reaction continued at 50°C for 15 min, THF (200 mL) was added, and N2 was bubbled into the flask for an additional 2–3 min. Then, the mixture was placed on a hot stirring plate (85°C) and stirred at 500 r/min for 2 days. Water was replaced every 8 hr to remove the unreacted species. Finally, the PCD-MCH was freeze-dried and subsequently characterized.

PCD-MCH was synthesized by radical polymerization of APTMACl. 0.05 g of MBA was first dissolved in 2.5 g of APTMACl with addition of 0.8 mL of deionized water. After all MBA was dissolved, 20 mL of TEMED, 0.3 g Fe3O4, and 0.5 g of PCD were added into the matrix. When the matrix was homogeneously mixed, 0.6 mL of saturated KPS solution was added. The reaction continued at 50°C in a water bath for 10 min. Then, the generated PCD-MCH was immersed in deionized water for 24 hr. PCD was obtained as a pale-yellow powder and subsequently characterized.

### 1.3. Batch adsorption experiment

The adsorption capacities of X-3B on PCD-MCH were evaluated via batch adsorption experiments. For the thermodynamics experiments, 15 mg PCD-MCH was added into 50 mL X-3B solution contained in a 100-mL FTFE bottle with stoppers, then the suspension was shaken on a thermostatic shaker at 150 r/min at 25 ± 1, 35 ± 1 or 45 ± 1°C for 24 hr until equilibrium was reached. Adsorption isotherms were obtained with the initial X-3B concentrations from 150 to 1500 mg/L. The effect of pH was tested with pH varying from 3.0 to 11.0. For the kinetic experiments, 0.3 g PCD-MCH was added into a 1000 mL X-3B solution with initial concentration of 600 mg/L and pH = 7.0 ± 0.2 at 25 ± 1, 35 ± 1 or 45 ± 1°C. Aliquots of the solution were withdrawn at various time intervals (2–1440 min) for further analysis. The effects of Cl, NO3, SO4, HCO3, PO4 and HA on X-3B removal were evaluated in batch tests with an initial X-3B concentration of 600 mg/L. The concentrations of co-existing anions or organics were set at 100, 300, and 500 mg/L, respectively (Qin et al., 2009). All samples taken from solution were immediately filtered through 0.45 μm polysulfone membranes.

Langmuir, Freundlich, and Sips models were employed to describe the adsorption isotherms. In order to evaluate the thermodynamic feasibility and further analyze the properties of the adsorption process, three basic thermodynamic parameters (ΔG°, ΔH° and ΔS°) were calculated. The pseudo-first-order model, pseudo-second-order model and Weber–Morris model were used to fit the adsorption kinetic data. The adsorption activation energy (Ea) was calculated by the Arrhenius equation. The detailed calculation formula is given in the Appendix A.

In addition, the Homogeneous Surface Diffusion Model (HSDM) was also used to simulate X-3B adsorption kinetics. In HSDM, the absorbent is assumed to be a homogeneous medium, and resistance from both external convective transport (or film) and intra-particle diffusion was considered, but the latter one was more important (Inglezakis et al., 2019). In fact, HSDM is a Fick’s second law-controlled diffusion model, which can be expressed as Eq. (1) in a 1-D spherical Cartesian coordinate system (Deng et al., 2019; Kim et al., 2016; Zhang et al., 2009):

$$\frac{\partial q_t}{\partial t} = \frac{1}{r^2} \frac{\partial}{\partial r} (D_r r^2 \frac{\partial q_t}{\partial r})$$

The initial and boundary conditions are given as,

$$\frac{\partial q_t}{\partial t} = 0, r = 0$$
$$q_t = q_e, r = R_p, t = \text{infinity}$$

where $q_t$ (mg/g) is the amount of adsorbed X-3B at any time t (min); $r$ (cm) and $R_p$ (cm) are the distance in radial direction of PCD-MCH particle and the diameter of PCD-MCH particle, respectively; $D_s$ (cm$^2$/min) is the intraparticle surface diffusion coefficient.

The average adsorbed concentration inside the adsorbent is,

$$q = \frac{3}{R_p^2} \int_0^{R_p} q(r,t)r^2 dr = \frac{(C_0 - C)V}{m}$$

where $m$ (g) is the mass of the adsorbent and $V$ (L) is volume of the X-3B solution.

### 1.4. Magnetic separation and recycling

After 24 hr adsorption of X-3B on PCD-MCH at initial concentrations of 100 and 1500 mg/L, the spent PCD-MCH was collected by a magnetic field. Then this powder was gently washed with 0.1 mol/L NaOH in ethanol for 24 hr at 25 ± 1°C, and further washed with 100 mL of deionized water. The regenerated PCD-MCH was used again in the next reuse–regeneration cycle.

### 1.5. Analysis and characterization methods

The residual X-3B in the filtrate was analyzed by UV–Vis spectroscopy. The surface charge of the adsorbent was measured using a Zetasizer Nano Z analyzer (Malvern, UK). Field emission scanning electron microscopy (FESEM; FEI, The Netherlands) and H8000 high resolution transmission electron microscopy (Hitachi, Japan) were used to analyze the surface morphology of the PCD-MCH. The magnetic properties of PCD-
MCH was tested using a vibrating sample magnetometer (VSM, 7037/9509-P, Lake Shore, Lake Shore Cryotronics Inc., USA). ATR-IR spectra (Vector 22 spectrophotometer, Bruker, Germany) were recorded at a resolution of 2 cm$^{-1}$ to characterize the synthesis process and changes in surface groups before and after adsorption. The valences of specific elements before and after adsorption were analyzed by XPS (PHI Quantera Spectrometer, USA). Curve fitting of the N 1s, S 2p and C 1s spectra was determined by a Gaussian–Lorentzian peak shape using the XPS Peak software 4.1 after Shirley background correction.

2. Results and discussion

2.1. PCD-MCH characterization

Fig. 1 presents the zeta potentials (ZP), magnetic hysteresis loop (VSM), ATR-IR spectral, SEM and TEM images of PCD-MCH, MCH and PCD. In Fig. 1a, as pH increased from 3.0 to 10.9, PCD-MCH maintained a positive surface charge, which could be attributed to the functional group (–N$^+$ (CH$_3$)$_3$) in the monomers of CH, thereby implying the presence of electrical attraction for anions (Palanisamy et al., 2016). Moreover, within the pH range of 3.0–8.0, the ZP values of PCD-MCH presented slight fluctuations, with the average value of 31.5 mV. As pH further increased up to 10.9, these values decreased to 16.7 mV. In comparison with MCH (Lo et al., 2011), the ZP values of PCD-MCH decreased by 6% under acidic and neutral conditions, while under alkaline conditions, the difference between them was insignificant. This implied that polycyclodextrin modification slightly reduced the positive ZP values of MCH within acidic and neutral pH. At alkaline pH, the shielding effects of OH$^-$ groups contributed to the decline of their ZP values and aforementioned differences.

Fig. 1b indicates that PCD-MCH was nearly superparamagnetic due to its weak hysteresis phenomenon. The saturation magnetization of around 3.8 emu/g proved that PCD-MCH was suitable for magnetic separation from aqueous solution (Xiao et al., 2013).

As shown in Fig. 1c, the ATR-IR spectra of PCD-MCH contained the spectral features of intact β-CD (Alsbai et al., 2016; Zhou et al., 2018), such as the stretches of O–H (3373 cm$^{-1}$), aliphatic C–H (2930 cm$^{-1}$), C–O–C (1155 cm$^{-1}$) and C–O (1030 cm$^{-1}$). This phenomenon implied that the integrity of the cavity structure of cyclodextrin was retained in PCD-MCH. Furthermore, the peaks at 1643 and 1548 cm$^{-1}$ were assigned to C–O and C–N stretching vibrations from both the monomer (APTMACL) and the crosslinker (MBA) respectively. The peak at 967 cm$^{-1}$ corresponded to the bending vibration of the trimethyl ammonium group [N$^+$ (CH$_3$)$_3$]. In addition, a characteristic Fe–O band appeared at 549 cm$^{-1}$, thereby proving the presence of Fe$_3$O$_4$ (Dong and Wang, 2016b; Hao et al., 2019; Ivashchenko et al., 2016).

The morphologies of MCH and PCD-MCH are shown in Fig. 1d–f. The surface morphology of PCD-MCH presented spheroidal aggregates (Fig. 1e), while MCH presented a pleated surface structure (Fig. 1d). This roughness difference could be caused by the poly-cyclodextrin modification. In the TEM image (Fig. 1f) of PCD-MCH, numerous small blocks were aggregated and provided large surface area.

![Zeta potentials of MCH, X-3B, and PCD-MCH (a); magnetic hysteresis loop (VSM) of PCD-MCH (b); ATR-IR spectra of MCH, PCD, and PCD-MCH (c); SEM micrographs of MCH (d), PCD-MCH (e); and TEM image of PCD-MCH (f).](image-url)
2.2. Adsorption isotherms

Fig. 2 shows the adsorption isotherms of X-3B uptake by PCD-MCH, MCH, and PCD at 150–1500 mg/L initial concentrations. At first, the adsorption capacities of PCD-MCH, MCH, and PCD increased sharply with increasing equilibrium concentration from 0 to 100 mg/L, and the three curves coincided. Then the adsorption capacity of PCD-MCH increased gradually and approached the plateau of 2792.3 mg/g at an X-3B equilibrium concentration of 351.1 mg/L. However, the adsorption capacities of MCH and PCD promptly shifted to stable values after rapid increase for X-3B equilibrium concentrations of 0–100 mg/L, and their maximum values were 2138.9 mg/g, 1820.8 mg/g, respectively. This result indicated that PCD modification improved the adsorption capacity of PCD-MCH at equilibrium concentrations above 100 mg/L. As shown in Table 1 comparing with the reported adsorbents our PCD-MCH had the highest capacity for X-3B, which indicated that PCD-MCH can serve as a promising candidate for the remediation of dye wastewaters.

The adsorption isotherms of PCD-MCH were fitted by Langmuir, Freundlich, and Sips models and the corresponding parameters are reported in Appendix A Table S2. The Sips model showed the best fitting result due to having the highest correlation coefficient ($R^2$). These results proved that the adsorption of X-3B on PCD-MCH could be described by the monolayer and multilayer synergistic adsorption model (Zeng et al., 2019).

The thermodynamic parameters for X-3B adsorption onto PCD-MCH were as following: $\Delta G^0$ at 298, 308, and 318 were $-17.39$, $-18.22$, and $-19.40$ kJ/mol, respectively, $\Delta H^0$ was 12.49 kJ/mol, and $\Delta S^0$ was 100.10 J/mol/K. The negative $\Delta G^0$ indicated that X-3B adsorption onto PCD-MCH was a spontaneous physical adsorption process (Li et al., 2017). The positive

![Fig. 2 — Adsorption isotherms of X-3B on MCH, PCD and PCD-MCH. Initial X-3B concentrations 150–1500 mg/L; adsorbent dose 0.3 g/L; total solution volume 50 mL; pH 7.0 ± 0.2; temperature 25 ± 1°C and shaking time 24 hr.](image)

Table 1 — A performance comparison between PCD-MCH and other adsorbents for X-3B removal from water.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>Concentration (mg/L)</th>
<th>Dose (g/L)</th>
<th>Adsorption capacity (mg/g)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(bipy) 3 (SO 4)In]n</td>
<td>1500</td>
<td>0.5</td>
<td>915</td>
<td>Xiao et al. (2015)</td>
</tr>
<tr>
<td>SBA-3</td>
<td>30</td>
<td>0.2</td>
<td>110</td>
<td>Anbia et al. (2010)</td>
</tr>
<tr>
<td>Tannin gel</td>
<td>40</td>
<td>0.4</td>
<td>45.25</td>
<td>Maria Rahman et al. (2014)</td>
</tr>
<tr>
<td>MFe 3 O 4/CS NPs</td>
<td>200</td>
<td>0.4</td>
<td>461.3</td>
<td>Cao et al. (2014)</td>
</tr>
<tr>
<td>NH 3 -MCM-41</td>
<td>92.3</td>
<td>0.5</td>
<td>209.2</td>
<td>Qin et al. (2009)</td>
</tr>
<tr>
<td>Ti-CSMIP</td>
<td>100</td>
<td>0.2</td>
<td>161.1</td>
<td>Deng et al. (2017)</td>
</tr>
<tr>
<td>CB [8]</td>
<td>300</td>
<td>0.2</td>
<td>1434.5</td>
<td>Li et al. (2017)</td>
</tr>
<tr>
<td>CTF</td>
<td>246</td>
<td>0.8</td>
<td>264.59</td>
<td>Wang et al. (2014)</td>
</tr>
<tr>
<td>Carbon aerogel</td>
<td>800</td>
<td>2</td>
<td>199</td>
<td>Wu et al. (2007)</td>
</tr>
<tr>
<td>PCD-MCH</td>
<td>600</td>
<td>0.3</td>
<td>1996.9</td>
<td>This study</td>
</tr>
</tbody>
</table>

Fig. 3 — Effect of content time on X-3B adsorption on PCD-MCH at initial X-3B concentrations of 600 mg/L. Insets: (a): adsorption kinetics linear fitting by pseudo-first-order model and pseudo-second-order model. (b): adsorption kinetics linear fitting by Weber–Morris intraparticle equation. PCD-MCH dose 0.3 g/L; total solution volume 1000 mL; pH 7.0 ± 0.2 and temperature 25 ± 1°C.
$\Delta H^0$ confirmed the endothermic nature of the adsorption process, and increasing temperature facilitated the X-3B adsorption. In addition, $\Delta H^0$ was in the range of 0–42 kJ/mol, this also indicated that the physical adsorption occurred without chemical bond formation (Hao et al., 2018).

2.3. Kinetics of X-3B adsorption on PCD-MCH

The adsorption kinetics of X-3B on PCD-MCH and parameters are shown in Fig. 3 and Appendix A Table S3. As shown in Fig. 3a, a rapid increase of adsorption capacity occurred within 4 hr, which reached 94.5% of the maximum capacity. Then the X-3B uptake rate approached equilibrium within 6 hr with maximum adsorption capacity 1996.9 mg/g.

As indicated in Fig. 3a, the pseudo-first-order kinetic model could better describe the adsorption process of X-3B by PCD-MCH than the pseudo-second-order kinetic model. The $E_a$ value based on the rate constant of pseudo-first-order adsorption kinetics was calculated as 9.08 kJ/mol. This implied that X-3B adsorption onto PCD-MCH occurred by physisorption due to the $E_a$ value being < 20 kJ/mol (Hao et al., 2018).

The fitting result of the Weber–Morris model for the adsorption kinetics showed that there were three linear regions (Fig. 3b) with respective slopes of 178.80, 10.62, and 0.92 (Appendix A Table S3), which implied that three consecutive mass transfer rate-controlling steps occurred during the above adsorption process: liquid film or external diffusion, intraparticle or internal diffusion, and access to the active sites of the interior surface (Luo et al., 2019; Okoli et al., 2014; Qin et al., 2009). The first linear portion of the plot had the steepest slope, corresponding to the initial rapid kinetics feature. At this diffusion stage, X-3B migrated from the bulk solution to the boundary layer surrounding the PCD-MCH particles, or across the boundary layer to the exterior surface of the PCD-MCH. The second linear portion had a lower slope, where X-3B continuously migrated from the exterior surface into the interior surface of PCD-MCH (Tan and Hu, 2017; Zeng et al., 2019), of which intraparticle or internal diffusion was dominant. The third linear portion was the final stage, where X-3B accessed the active sites on the interior surface of PCD-MCH and adsorption was completed. At this stage, the extremely low solute concentration in the solution restricted X-3B diffusion and it is universally acknowledged that slow
adsorption kinetics are caused by rate-limited diffusion mass transfer. As indicated in Fig. 3b, the plot did not pass through the origin, which implied that both boundary layer diffusion and intraparticle diffusion contributed to the rate-controlling step (Cheung et al., 2007; Tang et al., 2012).

Based on the fitting results of the W-M model, liquid film or external diffusion, intraparticle or internal diffusion, and accessing the active sites of the interior surface during X-3B adsorption on PCD-MCH were rate-limiting steps. Therefore, HSDM was suitable for the above kinetics simulation.

According to the method of Dong et al. (2015), the external mass transfer coefficient in the liquid phase ($k_l$) was determined first, which was $4.68 \times 10^{-8}$ cm/min at the initial X-3B concentration of 600 mg/L (Dong et al., 2015). In order to estimate the diffusion coefficient ($D_s$) through resolving the partial differential Eq. (1), FlexPDE 7.0 was adopted to couple Eq. (5). The corresponding HSDM simulation curve is shown in Fig. 3a, with a high coefficient of 0.996, and $D_s$ was

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**Fig. 5** Evolution of the dimensionless radial X-3B concentration profiles, $C_p$ versus $r$ inside the particle calculated from the HSDM batch adsorption model at initial X-3B concentrations of 600 mg/L. PCD-MCH dose, 0.3 g/L; total solution volume, 1000 mL; pH, 7.0 ± 0.2 and temperature, 25 ± 1°C.

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**Fig. 6** Effect of pH on X-3B adsorption and ZP values on PCD-MCH. Initial X-3B concentration, 600 mg/L; PCD-MCH dose, 0.3 g/L; total solution volumes, 50 mL; pH range, 3–10.5; temperature, 25 ± 1°C and shaking time, 24 hr.
$3 \times 10^{-11}$ cm$^2$/min at the initial X-3B concentration of 600 mg/L. In comparison with previous studies, this $D_s$ value was higher. This implied that the diffusion of X-3B inside the pores of PCD-MCH was faster.

Moreover, the adsorption capacity $q$ of PCD-MCH particles and the X-3B concentration $C_p$ within these particles at time $t$ and at any radial position $R$ was determined through above Eq. (5) coupling. The normalization of radial position $R$ to the 0 to 1 or $-1$ to 0 range was completed by dividing the average radius $R_P$ of the PCD-MCH particles. The X-3B adsorption capacity $q$ on PCD-MCH was normalized by dividing the adsorption capacity at equilibrium of $q_e$. The gradient chart of quotient values ($q/q_e$) was plotted in a two-dimensional profile (Fig. 4). Combined with the values of $n$ and $k_F$ in the Freundlich isotherm model (Appendix A Table S2), the variations of $C_p$ with time at any radial position $r$ were plotted in Fig. 5. Based on the visually illustrated charts, the adsorption capacity depletion kinetics could be divided into three stages. As adsorption time increased to 120 min, the color of the two-dimensional circle profile changed from complete dark blue at 20 min to a light blue ring at 30 min, a yellow ring at 60 min, and a red ring at 120 min; the corresponding $q/q_e$ reached 0.84 (Fig. 4). At this stage, Fig. 5 shows that the $C_p$ curves moved towards the radial position $r$ of 100 $\mu$m with a relatively high concentration gradient along the radius from 20 to 120 min, and the $C_p$ values at the radial position $r$ of 168 $\mu$m were about 31.01, 88.29, 146.27, and 131.48 mg/L at 20, 30, 60, and 120 min, respectively. The above visually observable variations indicated that X-3B in solution could rapidly transport to the surface of PCD-MCH, where surface diffusion occurred. After 100 min adsorption, $C_p$ in the outmost layer decreased, which indicated that the transport of X-3B towards the interior layers of PCD-MCH gradually took place. At the second stage, Fig. 4 shows that the color of the outer layer changed from red to dark red as the adsorption time increased from 120 to 480 min, the $q/q_e$ values
approached about 1.0 and saturation adsorption of X-3B on PCD-MCH the outer layer took place. Along the radius of PCD-MCH particles, the color of the two-dimensional profile gradually changed from dark red, to red, yellow and blue. At the end of this stage, most of the profile was dark red. Fig. 5 shows that the $C_p$ inside the PCD-MCH gradually increased, a noticeable change in $q/e_0 = 0$ occurred at 360–480 min, and this value was 11.53 mg/L at $q/e_0 = 0$ and 480 min. The X-3B transport at this stage was much slower than that at the surface diffusion stage; the former was dependent on intra-particle or internal diffusion. At the third stage, the area with dark red color almost covered the two-dimensional profile, and the area with less than 90% saturation adsorption remained at only about 12.5%. As indicated in Fig. 5, the $C_p$ at $q/e_0 = 0$ showed a large improvement as the adsorption time increased from 480 to 1200 min, and it could reach 45.20 mg/L at the end of this stage. In fact, the $C_p$ values along the radius of PCD-MCH particle also tended to about be 46 mg/L at this time. In addition, the $C_p$ gradient at this stage was lower than that at the second stage, which was controlled by access to the active sites of the interior surface.

### 2.4. Effect of pH on adsorption

The effect of pH on X-3B uptake by PCD-MCH is shown in Fig. 6, and the variation of ZP with pH was also measured for comparison. As pH increased from 3.0 to 6.0, the X-3B adsorption capacity on PCD-MCH maintained a relatively stable value of 2002.7 mg/g, and then a slight increase in this capacity took place when pH increased from 6.0 to 7.0 with the maximum adsorption capacity (2060.3 mg/g). Afterwards, the adsorption capacity gradually decreased to 1928.1 mg/g at pH = 10. As pH further increased, a sharp decrease occurred. The variation trends of the adsorption capacity and ZP of PCD-MCH were similar, which implied that the X-3B adsorption on PCD-MCH was controlled by electrostatic attraction. In addition, the effect of solution pH on the surface charge of PCD-MCH and on the form of the X-3B dye molecule (Zhang et al., 2014) could cause some differences between their varying trends.

At acidic pH, two sulfuric groups in the X-3B molecule (Appendix A Table S1) were ionized, then X-3B became negatively charged. The permanent positive charge of the quaternary amino group in PCD-MCH could strongly attract the X-3B molecule onto its surface. Within the pH range of 3.0–5.0, the parallel curves for adsorption capacity and ZP proved that adsorption was due to electrostatic attractive interaction. As pH rose from 5.0–7.0, the reduction in ZP of PCD-MCH did not lead to a decrease in the X-3B adsorption capacity; its slight elevation implied that other attractive interactions also took place, such as hydrogen bonds between the hydroxyl groups in PCD-MCH and the X-3B molecule, and the Van der Waals force among adsorbed molecules (Zhang et al., 2014). In addition, the neutral forms of hydroxyl groups could offset the electrostatic repulsion interactions between protonated hydroxyl groups in the X-3B molecule and the positively charged surface of PCD-MCH (Haldorai and Shim, 2014; Wang et al., 2019). As pH increased to alkaline conditions, the ZP of PCD-MCH decreased and competition by hydroxyl groups contributed to a reduction in the adsorption capacity of PCD-MCH for X-3B. This phenomenon became more serious as pH rose above 10.0 (Crini, 2003; Ozmen et al., 2008; Zhao et al., 2015).

The stable capacity above 2000 mg/g obtained within a wide pH range from 3.0 to 9.0 indicated that PCD-MCH had stable adsorption ability towards X-3B.

### 2.5. Effect of co-existing ions and HA

The effects of the potentially competitive anions Cl$^-$, NO$_3^-$, HCO$_3^-$, SO$_4^{2-}$, PO$_4^{3-}$ and HA on X-3B adsorption by PCD-MCH were investigated as illustrated in Fig. 7. As indicated in Fig. 7, less than 5% reduction in the adsorption capacity of X-3B occurred in the presence of Cl$^-$, NO$_3^-$, or HCO$_3^-$, of which the effect of Cl$^-$ was almost negligible. However, the presence of SO$_4^{2-}$, PO$_4^{3-}$ or HA had some effect on the adsorption capacity of X-3B, and the capacity reduction varied in the order PO$_4^{3-} >$ SO$_4^{2-} >$ HA$^-$. Even at 500 mg/L co-existing PO$_4^{3-}$, the adsorption capacity only decreased to 92.8%. Similar to X-3B, PO$_4^{3-}$ and SO$_4^{2-}$ had negative charge and electrostatic attraction to PCD-MCH, but they could not be encased in the cavity of PCD partly due to their small size, thus their presence only resulted in less than 10% reduction in the X-3B adsorption capacity. In addition, HA has more phenyl groups and oxygen-containing groups than X-3B, and its size is larger, so HA only showed slight competition with X-3B on adsorption due to the inclusion interaction of β-CD.

Based on the aforementioned comparisons, PCD-MCH showed good selectivity towards X-3B, suggesting its potential for practical utilization in dye wastewater treatment.

### 2.6. X-3B desorption and reuse

Fig. 8 presents the recycling behavior of spent PCD-MCH. At 100 mg/L X-3B initial concentration, the regenerated PCD-MCH maintained 93.1% the adsorption capacity of fresh PCD-MCH after five adsorption–desorption cycles (Fig. 8a). At 1500 mg/L X-3B initial concentration, after three cycles, the
adsorption capacity was 40% with a value of 892.7 mg/g, which was still higher than most of the reported adsorbents (Cao et al., 2014; Li et al., 2017; Wang et al., 2014). At low initial concentration, the adsorbed X-3B only occupied adsorption sites on PCD-MCH that could be easily desorbed by NaOH–ethanol; thus, the interactions between X-3B and these sites were essentially reversible. However, at high X-3B initial concentration, the internal diffusion resistance (Afkhami et al., 2010;
Daneshvar et al., 2017; Kyzas et al., 2012; Luo et al., 2019; Okoli et al., 2014) and strong hydrogen bonding (Mura, 2014) between X-3B and some of the active sites could inhibit X-3B desorption by NaOH-ethanol. Therefore, in future research, the reagents for desorption need to be optimized.

2.7. Adsorption mechanisms

2.7.1. ATR-IR

The ATR-IR spectra of PCD-MCH before and after X-3B adsorption are compared in Fig. 9. Three major peaks appeared for X-3B-absorbed PCD-MCH in the regions of 1151, 1385 and 1597 cm\(^{-1}\), corresponding to C–O (on the phenoxide), N=N (in the azo group) and C=N (between the azo group and phenyl ring), respectively, which indicated that X-3B was successfully adsorbed on PCD-MCH (Park, 2005). The X-3B-absorbed PCD-MCH showed peaks at 1184 and 1038 cm\(^{-1}\), which were assigned to the S=O stretching vibrations of the SO\(^3^-\) group in the X-3B molecule (Yilmaz et al., 2010). Furthermore, the bathochromic shift of \(\nu(OH)\) from 3373 to 3354 cm\(^{-1}\) and the broadening of the peak can be attributed to the weakening of hydrogen bonds in cyclodextrin molecules and the formation of intermolecular hydrogen bonds with X-3B (Zhao et al., 2015). The strength of the bands at (967 cm\(^{-1}\)) of aromatic groups of X-3B entering into the CD cavity (Zhao et al., 2015; Xu et al., 2016). The attraction and hydrogen bonding (Karthika and Vishalakshi, 2018) as well as enough active binding force for X-3B, such as electrostatic attraction and hydroxyl groups on the surface of PCD-MCH could provide enough active binding force for X-3B, such as electrostatic attraction and hydrogen bonding (Karthika and Vishalakshi, 2015; Xu et al., 2016).

2.7.2. XPS analysis

The chemical compositions of PCD-MCH before and after X-3B sorption were further probed by XPS analyses shown in Appendix A Fig. S1, and the S 2p, N 1s, C 1s and O 1s spectra are shown in Fig. 10.

The enhanced S 2p peaks in the XPS spectrum are shown in Fig. 10a. The content of SO\(^3^-\) increased, which indicated that X-3B had been successfully adsorbed on PCD-MCH. As shown in Fig. 10b–c, the N 1s XPS spectra for fresh PCD-MCH distinctly showed two states of nitrogen, C=N/N=N (399.4 eV) and –[N\(^+\)(CH\(_3\))\(_3\)] (402.3 eV), which belonged to MCH in PCD-MCH. After X-3B adsorption, the relative content of nitrogen in –[N\(^+\)(CH\(_3\))\(_3\)] was reduced from 25.0% to 13.2% and that in pyrrole-like nitrogen increased (from 75.0% to 86.8%) (Table 2). The increase of C=N group (399.4 eV) intensity indicated that X-3B was successfully adsorbed on PCD-MCH. It was also confirmed that –[N\(^+\)(CH\(_3\))\(_3\)] in PCD-MCH contributed to X-3B adsorption, which matches the decrease of the intensity of the –[N\(^+\)(CH\(_3\))\(_3\)] band (967 cm\(^{-1}\)) and the enhancement of the C=N band (1597 cm\(^{-1}\)) in the ATR-IR spectrum after adsorption (Dong and Wang, 2016a; Dong et al., 2017).

Fig. 10d–e shows the high-resolution C 1s spectra before and after X-3B adsorption. The deconvolution of the C 1s peak produced four peaks of binding energies 284.7, 285.3, 286.2, and 288.7 eV, respectively. These peaks corresponded to carbon atoms in the forms of C–C (aromatic), C–C (C–C=O, acyl), C–O (alcoholic hydroxyl ether), and C=O (O=C–OH, carboxyl and ester) (Badruddoza et al., 2011; Giesbers et al., 2011; Mura, 2014) and strong hydrogen bonding (Mura, 2014) between the azo group and phenyl ring, respectively, which indicated that X-3B-absorbed PCD-MCH showed peaks at 1184 and 1038 cm\(^{-1}\), which were assigned to oxygen atoms in the forms of C=O and C=O–H (H–O–H) respectively (Wen et al., 2015). The carbon content in the form of C–O groups decreased from 21.0% to 17.1% (%). In addition, the peak of carbon in the form of C–O increased (49.3%–63.6%) (Table 2). These changes indicated that the adsorption of X-3B by PCD-MCH is partly due to the adsorption of –OH, and hydrogen bonds may be formed during the adsorption process, which was consistent with the ATR-IR results.

Table 2 – Binding energy and relative content of N 1s, C 1s and O 1s in adsorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Valence state</th>
<th>Proposed component</th>
<th>Binding energy (eV)</th>
<th>Relative content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCD-MCH (before adsorption)</td>
<td>C 1s</td>
<td>C–C (aromatic)</td>
<td>284.7</td>
<td>49.3%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C–C (C–C=O, acyl)</td>
<td>285.3</td>
<td>2.4%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C–O (alcoholic hydroxyl ether)</td>
<td>286.0</td>
<td>21.0%</td>
</tr>
<tr>
<td></td>
<td>N 1s</td>
<td>N=N=N quaternary nitrogen</td>
<td>399.4</td>
<td>75.0%</td>
</tr>
<tr>
<td></td>
<td>O 1s</td>
<td>O=O–H (H–O–H)</td>
<td>533.3</td>
<td>81.8%</td>
</tr>
<tr>
<td>PCD-MCH (after adsorption)</td>
<td>C 1s</td>
<td>C–C (aromatic)</td>
<td>284.7</td>
<td>63.6%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C–C (C–C=O, acyl)</td>
<td>285.3</td>
<td>4.6%</td>
</tr>
<tr>
<td></td>
<td>N 1s</td>
<td>N=N=N quaternary nitrogen</td>
<td>399.4</td>
<td>86.8%</td>
</tr>
<tr>
<td></td>
<td>O 1s</td>
<td>O=O–H (H–O–H)</td>
<td>533.3</td>
<td>51.6%</td>
</tr>
</tbody>
</table>

3. Conclusion

A novel magnetic cationic hydrogel modified by poly-cyclodextrin (PCD-MCH) was synthesized. The maximum
value of the X-3B adsorption capacity was 2792.3 mg/g at an X-3B equilibrium concentration of 351.1 mg/L and pH = 7.0, which outperformed many reported adsorbents. Adsorption kinetics experiments indicated that 94.5% of the maximum X-3B adsorption capacity was achieved within 4 hr. The pseudo-first-order model, Weber–Morris model and HSDM could fit the adsorption kinetic data well, and the adsorption process was divided into three stages: surface or film diffusion within 0–120 min, intra-particle or wide mesopore diffusion within 120–480 min, and narrow mesopore/micropore diffusion within 480–1200 min. At the initial X-3B concentration of 600 mg/L, the diffusion coefficient (D_d) was $3 \times 10^{-11}$ cm$^2$/min. PCD-MCH maintained a high adsorption capacity for X-3B within the pH range of 3.0–10.0. Moreover, PCD-MCH had strong resistances against co-existing ions and HA, which could further support its practical utilization in wastewater treatment. Regeneration experiments demonstrated that PCD-MCH could be recycled with NaOH–ethanol. The ATR-IR and XPS spectra showed that the mechanisms of electrostatic interaction, the inclusion of cyclodextrin, and hydrogen bonding contributed to the X-3B adsorption process on PCD-MCH. This study indicated that PCD-MCH is a reusable adsorbent with pH stability and high adsorption capacity towards X-3B from dye-contaminated waters.

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**Appendix A. Supplementary data**

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jes.2019.09.008.

**REFERENCES**


