Preparation of polymeric silica composites through polydopamine-mediated surface initiated ATRP for highly efficient removal of environmental pollutants

Qiang Huang^{a,#}, Meiyong Liu^{a,#}, Qing Wan^a, Ruming Jiang^a, Liucheng Mao^a, Guangjian Zeng^a, Hongye Huang^a, Fengjie Deng^{a,*}, Xiaoyong Zhang^{a,*}, Yen Wei^{b,*}

^a Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

^b Department of Chemistry and the Tsinghua Center for Frontier Polymer Research, Tsinghua University, Beijing, 100084, P. R. China.

These authors contributed equally to this work

Xiaoyong Zhang; Email: xiaoyongzhang1980@gmail.com

Abstract

In this study, we developed a new procedure to prepare monodispersed functionalized SiO₂ (SiO₂-PDA-PDMC) composites via mussel inspired chemistry and surface initiated atom transfer radical polymerization (SI-ATRP). Samples were characterized by transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA) measurements. TEM results showed that spherical morphology was unchanged after the functionalization. FT-IR results confirmed the successful modification with polydopamine (PDA) and the presence of poly-([2-(Methacryloyloxy) ethyl] trimethylammonium chloride) (PDMC) layer on the surface of SiO₂ spheres. TGA data showed that the PDMC account for about 12.12 wt.% in the sample of SiO₂-PDA-PDMC composites. The XPS analysis further confirmed the existence of PDMC on the surface of SiO₂-PDA-PDMC composites. The obtained SiO₂-PDA-PDMC composites were used as adsorbent for the removal of Congo red (CR) from aqueous solution to evaluate the performance in environment application. The effect of contact time, solution pH, initial CR concentration and temperature on the adsorption of CR onto SiO₂-PDA-PDMC composites was investigated. Adsorption results demonstrated that adsorption of CR onto SiO₂-PDA-PDMC composites was a fast and efficient process. The adsorption equilibrium reached within 60 min, and the adsorption process followed the pseudo-second-order model. The experimental data of isotherms were better described by the Freundlich model. Thermodynamic study depicted the endothermic nature of adsorption and the process was spontaneous. Results from the effect of solution pH on the CR adsorption showed that the acidic condition favors the adsorption and provided evidence for the contribution of PDMC on the SiO₂-PDA-PDMC composites in the removal of CR. This study suggests SiO₂-PDA-PDMC composites can be developed as a new adsorbent for the removal of anionic dyes from aqueous solution.

Key words: Surface initiated atom transfer radical polymerization; Mussel inspired chemistry; Functionalized SiO₂ composites; Congo red removal.

1. Introduction

Dyestuff pollution is one of the most serious environmental problems today and removal of these dyestuff from wastewater has become one of the centre topic in environmental protection and remediation [1-5]. Congo red (CR) is a kind of typical benzidine azo dye (The structure is shown in **Scheme. 1**). It is widely used in textile, paper, biological dye and other fields because of its low cost, ease to use and stable chemical properties [6-8]. However, CR is also a kind of dye pollutant, which is harmful to human beings and environment. The intake of CR into human bodies can cause cancers and other long-term illnesses. Due to its good solubility, CR can be easily taken into water through the rain wash and industrial wastewater discharge. The existence of CR can restrict oxygen and light flow to the water and threaten the survival of aquatic organism [9,10]. Therefore, it is necessary to develop efficient treatment methods for the removal of CR from waste effluents. Some physical and chemical methods, such as coagulation/flocculation [11], filtration [12], oxidation [13-20], micellar enhanced ultrafiltration [21], adsorption [22-26], microbial degradation [27] have been used to remove dye pollutants. Adsorption is one of the most widely used methods due to its easy operation, cost effectiveness and high efficiency. For the method of adsorption, the adsorption capability of adsorbents is the key factor.

Scheme 1 The chemical structure of Congo red.

Recent years, the polymer-inorganic composite has been a research focus in the wastewater treatment. Bilge Erdem and colleagues [28] have reported the preparation of polymer/bentonite nanocomposites via in situ free radical suspension polymerization using a methacrylate based quaternary ammonium monomer ([2-(methacryloyloxy) ethyl]dimethyl-hexadecylammonium bromide). The prepared polymer/clay nanocomposites exhibited excellent adsorption performance for the removal of reactive black 5. Liu et al [29] have reported that quaternary ammonium polyethylenimine modified silica nanoparticles and used as adsorbents to remove methyl orange from aqueous solution. In this study, we choose the monodispersed SiO_2 and poly-([2-(Methacryloyloxy) ethyl] trimethylammonium chloride) (PDMC) as the materials to prepare polymer-inorganic composites. The monodispersed SiO_2 is a kind of environmental friendly material [30,31]. Due to their small size, high specific surface area, high chemical purity and good dispersibility, the monodispersed SiO_2 can be used as promising materials for the wastewater treatment. PDMC is a kind of cationic polymer with good water solubility [32]. The PDMC with rich cationic groups is very easily to attract anionic pollutants in aqueous solution through the strong electrostatic interaction. Thus, the adsorption efficiency of this kind of silica adsorbents would have an obvious enhancement after the incorporation of PDMC into

monodispersed SiO_2 . Surface initiated atom transfer radical polymerization (SI-ATRP) is a widely used method for the surface functionalization of inorganic materials. Wang et al [33] have reported the fabrication of hybrid silica nanoparticles using the method of SI-ATRP. Jia et al [34] have reported the synthesis of hybrid inorganic/organic nanocomposite electrolytes silica–poly(PEGMA-475) and silica–poly(PEGMA-1100) through the method of SI-ATRP. However, there is a small number of available groups on the surface of monodispersed SiO_2 to achieve the immobilization of initiator [35]. Hence, it is important to develop an efficient method for the surface modification of monodispersed SiO_2 .

Mussel inspired Chemistry is a newly emerging surface modification strategy. It is firstly reported from Herbert Waite's research of marine mussel adhesion in 1980s [36]. The method is to form a layer of multifunctional polydopamine (PDA) coatings via dopamine self-polymerization in an aqueous solution of dopamine.[37,38] The PDA coating can be used as a secondary reaction platform for the further functionalization. Due to its simple operation, low equipment requirement, and multifunction, mussel inspiration chemistry has been widely used in various fields [39-42]. Gao et al [43] have reported a one-step method for the preparation of PDA functionalized graphene hydrogel and the adsorption capacity of PDA-GH for different kinds of pollutants was greatly enhanced in comparison with HT-GH. Myung-Hyun Ryou et al [44] have reported a simple PDA coating process improved a variety of critical properties of separators for high power Li-ion batteries. More recently, Zhou et al have found that the PDA thin films can be used for surface grafting of polymers through light initiated surface polymerization.[45] Therefore, it is possibly obtained the different polymeric composites through the combination of mussel inspired chemistry and surface initiated polymerization. Considering many advantages of the method, mussel inspired chemistry can be in combination with SI-ATRP for the surface functionalization of the monodispersed SiO_2 with different polymers.

In this paper, we developed a new procedure for the preparation of functionalized monodispersed SiO_2 composites (shown as **Scheme. 2**). Firstly, the as-prepared monodispersed SiO_2 particles were modified with PDA. The PDA coating provided a versatile platform for secondary reactions. Then, the immobilization of initiator was achieved through the esterification reaction between the hydroxyl and amine groups of PDA and Bromoisobutryl bromide. The surface polymerization of PDMC was initiated using the method of SI-ATRP in aqueous solution. The obtained samples were characterized by transmission electron microscope (TEM), Fourier transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and thermal gravimetric analysis (TGA) measurements. Batch experiments were carried out to investigate the adsorption behavior of the functionalized SiO_2 composites to CR from aqueous solution. The adsorption kinetics, isotherms and thermodynamics were investigated in order to gain a deeper understanding of the adsorption process. Compared to the previous work [46,47], the method used in this study provides a versatile toolbox for preparation of various polymers with precisely controlled macromolecular architectures and well-controlled molecular weights. And it can be conducted in aqueous solution, which is in favor of the polymerization of ionic monomer. Besides, the ligand used in this study is more affordable than that of SET-LRP. For the SiO_2 -PDA-PAA in previous report[46], the preparation of the adsorbent is achieved by the grafting-to approach. In this study, the strategy for the preparation of the adsorbent is classified into grafting-from approach. In general, the grafting-to approach has a limit on grafting density, as

macromolecules already grafted to the surface hinder the attachment of further chains. For the grafting-from approach, single monomers can readily be incorporated into much more densely packed growing chains [48]. Therefore, this work offers a promising technology for the facile fabrication of positive charged adsorbents for anionic dyes removal. Considering these advantages of the strategy used in this study, it is expected to be applied in the construction of desired materials with high adsorption capacity for environment treatment.

Scheme 2 Schematic illustration of the preparation of monodispersed functionalized SiO₂ (SiO₂-PDA-PDMC) composites via the combination of mussel inspired chemistry and SI-ATRP.

2. Experimental section

2.1. Materials and methods

2.1.1. Materials

Tetraethyl orthosilicate (TEOS) (>99%), Ammonia solution (25-28%), Tris (chydroxymethyl) aminethane (Tris) (>99.9%), α-Bromoisobutyryl bromide (BiB) (98%), Cuprous bromide (CuBr) (99.0%) N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA) (99%), Congo red (CR) (CP), Triethylamine (TEA) (99.0%), and [2-(Methacryloyloxy) ethyl] trimethylammonium chloride solution (75 wt. % in H₂O) (DMC) were obtained from Aladdin Industrial Co., Ltd. (Shanghai, China). The dopamine hydrochloride (DA) was purchased from Sangon Biotech Co. Ltd. (Shanghai, China). And other reagents were analytical pure grade and all them were used without further purification.

2.1.2. Synthesis of adsorbent

The SiO₂ spheres were prepared via a modified Stöber method as described previously [30]. Typically, 24.75 mL H₂O, 61.75 mL ethyl alcohol and 4.5 mL TEOS were mixed in a 250 mL flask with intensively stirring. And then, 9 mL ammonia solution

(25-28%) was rapidly added into the TEOS solution under stirring. After reaction for 6 hrs at room temperature, the product was centrifugally separated from the suspension and washed with ethanol several times. The SiO₂ spheres were obtained after drying in vacuum oven at 333 K.

The surface modified SiO₂ (SiO₂-PDA) particles were synthesized using mussel inspired modification[49] as previously reported [46,47]. 1.5 g SiO₂ and 1.5 g DA were added into a 300 mL (10 mM) Tris buffer solution (pH 8.5) firstly, the mixture was sonicated for 20 min. And then, the homogeneous solution was stirred steadily at room temperature for 8 hrs. After reaction finished, the product was washed with ethanol several times and dried it at 333 K in a vacuum oven.

The functionalized SiO₂ particles with bromo groups (SiO₂-PDA-Br) were prepared through the esterification or acylation between BiB and hydroxyl or amine groups on the surface of SiO₂-PDA particles[50]. The detailed procedure is shown as follows: 1.5 g SiO₂-PDA was added into 30 mL dried toluene, the mixture was sonicated for 10 min to produce a homogeneous SiO₂-PDA suspension. Subsequently, a mixture of BiB (0.5 g) and dried toluene (10 mL) was quickly added into the SiO₂-PDA suspension with stirring and cooling. Then, 1.5 mL TEA was added dropwise into the system. After stirring for 2 hrs in ice bath, the obtained SiO₂-PDA-Br particles were washed with dried toluene and dried in vacuum oven at 333 K.

The graft polymerization of the cationic polymer PDMC onto SiO₂ (SiO₂-PDA-PDMC) was carried out in aqueous medium using SI-ATRP [51,52]. The initiator SiO₂-PDA-Br (1.5 g), monomer DMC (6.0 g) and catalyst CuBr (312.1 mg, 2.175 mmol) were mixed in 80 mL methanol-water (1:3) solution aided by sonication for 10 min to form a homogeneous suspension. The mixture was degassed and backfilled with nitrogen five times and kept under nitrogen atmosphere. Subsequently, the ligand PMDETA (376.9 mg, 2.175 mmol) was injected into the suspension with stirring and reacted in oil bath at 353 K for 24 hrs. After the polymerization was complete, the product was centrifuged with 10000 r/min for 10 min and washed with EDTA solution and deionized water several times to remove free untethered polymers and catalytic system compounds. Finally, the obtained SiO₂-PDA-PDMC composites were dried at 333 K under vacuum.

2.2. Characterization and instruments

FT-IR spectra were measured on a Nicolet 5700 Fourier transform spectrometer instrument (Nicolet Instrument Company, USA) with resolution and scans number of 4 and 32 cm⁻¹, respectively, in the range of 4000-400 cm⁻¹. TEM images were taken with a JEM-2100 transmission electron microscope (Japan Electron Optics Laboratory Co., Ltd.). TGA data were obtained using a SDTQ600 thermo gravimetric analyzer instrument (TA Instruments, Water LLC. USA) in the range of 298-1073 K under N₂ atmosphere. The chemical compositions of functionalized SiO₂ composites was determined by the technology of XPS and XPS measurements were carried out by using a VGESCALAB 220-IXL spectrometer with Al K α X-ray source (Thermo Fisher Scientific Inc. USA). The zeta potential of the SiO₂-PDA-PDMC was measured using a Malvern Zetasizer Nano ZS instrument (Malvern instrument) in 1 mmol/L NaCl solution. The pH was adjusted using 0.1 mol/L HCl aqueous solution or 0.1 mol/L NaOH solution.

2.3. Adsorption study

The adsorption of CR in aqueous solution on the SiO₂-PDA-PDMC composites was investigated with batch experiments. Adsorption kinetic experiments were performed by adding 10 mg adsorbent into a beaker containing 50 mL 50 mg/L CR solution at room temperature. The contact time was varied between 0 and 60 min. After a predetermined contact time, the mixture was centrifuged with 8000 r/min for 1 min to remove solid adsorbent and the clear supernatant solution was submitted for determination. The equilibrium isotherm studies were conducted with different initial CR concentrations (range from 25 to 300 mg/L) at room temperature (299 K). The test beakers were shaken for 60 min to get equilibrium state. At the end of adsorption, the solid adsorbent was separated by centrifugation for 8000 r/min and the supernatant solution was diluted to predetermined volume with deionized water for the further determination. The effect of temperature on CR adsorption was studied at six different temperatures (299, 303, 313, 323, 333 and 343 K) with fixed amount of adsorbent (10 mg) in 50 mL 50 mg/L CR solution. The influence of solution pH on the CR removal was also investigated by adding defined amount the SiO₂-PDA-PDMC adsorbents into 50 mL of same concentration CR solution with different solution pH values ranging from 6 to 10. The values of solution pH were adjusted by adding the HCl aqueous solution or NaOH solution as mentioned above. After adsorption, those obtained supernatants were analyzed using an ultraviolet and visible spectrophotometer (TU-1810, Beijing) by monitoring the absorbance changes at a λ_{max} of 498 nm for the residual CR concentrations.

The amount (Q_t) (mg/g) (1) of adsorbed CR at time t (min) and the equilibrium adsorption capacity (Q_e) (mg/g) (2) were calculated based the mass balance equations as given below:

$$Q_t = \left(\frac{C_0 - C_t}{m} \right) \times V \quad (1)$$

$$Q_e = \left(\frac{C_0 - C_e}{m} \right) \times V \quad (2)$$

Where C_0 (mg/L) is the initial concentration of CR in the solution; C_t (mg/L) and C_e (mg/L) represent the t time and equilibrium concentrations of CR solution, respectively; m (mg) is the dry weight of the adsorbent; and V (mL) is the volume of the CR solution.

3. Results and discussion

3.1. Characterization of the adsorbent

Fig. 1 shows TEM images of SiO₂ particles before and after being functionalized with the cationic polymer PDMC. As shown in **Fig. 1A**, the sample of pure SiO₂ exhibits a spherical morphology without aggregation. By measuring the diameter of SiO₂ particles from the TEM images, it can be observed that the size of SiO₂ particles is in the range of 310-380 nm. Besides, the sample of pure SiO₂ is white powder after drying. When the SiO₂ particles were further functionalized with cationic polymer PDMC via the method of mussel inspired modification and SI-ATRP, the obtained products still kept the spherical morphology (**Fig. 1B**). The result suggests that the modification of mussel inspiration and SI-ATRP have no effect on the structure of SiO₂

particles. As is clear from the **Fig. 1B**, a layer of coating appeared on the surface of SiO₂ particles, and the size of SiO₂-PDA-PDMC particles is in the range of 380-430 nm. In comparison with the pure SiO₂, the particle size and surface roughness of SiO₂-PDA-PDMC increased. By measuring the diameters of the core and shell from the high magnification TEM pictures, the thickness of polymer shell is calculated to be around 35 nm. These results provide obvious evidence for the successful functionalization. In addition, the sample of SiO₂ turned into deep brown after being functionalized with PDA and PDMC.

Fig. 1 TEM images of pure SiO₂ (A) and cationic polymer PDMC grafted SiO₂ particles (B).

In order to gain a deeper understanding of the characteristics of SiO₂ before and after being functionalized, FT-IR spectrometer was applied to detect the changes in chemical bonds. The FT-IR spectra of SiO₂, SiO₂-PDA-Br and SiO₂-PDA-PDMC are shown in **Fig. 2A**. For pure SiO₂, the peaks at 1097, 950, 795 and 457 cm⁻¹ are attributed to the Si-O-Si stretching and bending vibration, Si-OH vibration, Si-O-Si symmetric stretching vibration and Si-O stretching vibration, respectively. The peaks at 3641 and 1643 cm⁻¹ are related to the vibrations of water molecules [53]. After the surface modification with PDA and immobilization of initiator, several new peaks are observed on the spectrum of SiO₂-PDA-Br. The peaks at 2926 and 2743 cm⁻¹ are assigned to the C-H stretching vibration. The band at 1610-1450 cm⁻¹ is ascribed to the -C=C- benzene skeletal vibration. Besides, there are two weak peaks at 1736 and 594 cm⁻¹ contribute to the presence of C=O group of ester and C-Br band respectively. These results demonstrate the successful surface modification with PDA and the initiator has been immobilized on the surface of SiO₂ particles. For SiO₂-PDA-PDMC, the strong peak at 1483 cm⁻¹ is the characteristic absorption of quaternary-N [54]. The intensification of -CH₂ adsorption peaks (observed at 2926 and 2858 cm⁻¹) has a phenomenal increase and the peaks become sharper after being functionalized with PDMC. These results confirm the existence of PDMC chains on the surface of SiO₂ particles. In addition, there is a remarkable increase of the adsorption peak intensity at 1732 cm⁻¹ after the functionalization. It could be the result of the vibrating absorption of carbonyl groups in the grafted PDMC.

Fig. 2 FT-IR spectra of SiO₂, SiO₂-PDA-Br and SiO₂-PDA-PDMC (A); TGA curves of SiO₂, SiO₂-PDA-Br and SiO₂-PDA-PDMC (B).

TGA was used to study the thermal stabilities of SiO₂, SiO₂-PDA-Br and SiO₂-PDA-PDMC particles and estimate the amount of PDA-Br and PDMC in SiO₂-PDA-PDMC composites. The TGA curves of SiO₂, SiO₂-PDA-Br and SiO₂-PDA-PDMC are shown in **Fig. 2B**. As for these samples, the weight loss before 433 K contributes to the dehydration of the adsorbed water or moisture. The residual mass percent of pure SiO₂, SiO₂-PDA-Br and SiO₂-PDA-PDMC particles are 90.01 wt.%, 77.80 wt.% and 64.98 wt.%, respectively, at 1062 K. The weight loss of pure SiO₂ is calculated to be 3.93 wt.% (except water). The low value of weight loss at high temperature confirms the excellent thermal stability of SiO₂. After the immobilization of initiator, the weight loss of SiO₂-PDA-Br is found to be 15.39 wt.%. The increase of weight loss in the range of 433-1062 K is attributed to the decomposition of organic component. According to the TGA data, the amount of PDA-Br is estimated to be about 11.46 wt.%. For SiO₂-PDA-PDMC, it is clear that the thermal degradation process has three stages. The first stage between 300 K and 433 K is associated with the thermal decomposition of adsorbed water. The second stage occurred in temperature range from 433 to 618 K with weight loss about 20.95 wt.%. This significant weight loss may be the result of the decomposition of the polymer chain and other organic compounds. The final stage is observed between 618 and 1062 K. The weight loss (6.55 wt.%) is attributed to the thermal decomposition of inorganic compounds on the SiO₂-PDA-PDMC composites. From the change of weight percentage in TGA data, it can be estimated that the amount of polymer PDMC on SiO₂-PDA-PDMC composites is about 12.12 wt.%. These results provide more evidence that SiO₂ particles have been successfully functionalized with PDMC.

Fig. 3 XPS wide scan (A) and narrow scan spectra of SiO₂-PDA-PDMC: C1s (B); N1s (C); O1s (D); Si2p (E); Cl2p (F).

XPS is an effective technology to investigate the surface chemical compositions of the functionalized SiO₂ composites. The XPS wide scan spectrum of SiO₂-PDA-PDMC is shown **Fig. 3A**. It can be observed that the characteristic signals of carbon (C1s at 284.80 eV), nitrogen (N1s at 399.80 eV), oxygen (O1s at 532.38 eV), silica (Si2p at 102.22 eV) and chlorine (Cl2p at 198.30 eV) are all detected. The thickness of polymer layer is about 35 nm, as determined by TEM, leading to the feeblish signal of silica. These data indicate the polymer of PDMC and PDA have been introduced on the SiO₂ surface. In addition, the narrow scan spectra and curve fitting for the sample of SiO₂-PDA-PDMC are studied and shown in **Fig. 3B-F**. The deconvolution of C1s core-level spectrum (**Fig. 3B**) results in four peaks at 284.79, 285.50, 286.20 and 288.70 eV, which are ascribed to C-C, C-N, C-O/C-N(CH₃)₃⁺ and O-C=O, respectively. The N1s spectrum (**Fig. 3C**) is resolved into two typical peaks at 399.79 and 402.80 eV, associated with the amine (-N-) and quaternary ammonium cations (N(CH₃)₃⁺) of PDMC[55], respectively. Moreover, the XPS O1s core-level spectrum (**Fig. 3D**) consists of three peak components with BEs at 531.50, 532.40 and 533.40 eV, which are assigned to Si-O, C=O and -OH from SiO₂, side chains of PDMC and catechol and quinine of PDA[56,57], respectively. Two peaks at 102.23 and 103.53 eV from Si2p spectrum (**Fig. 3E**) are contributed to Si2p_{1/2} and Si2p_{3/2} [58]. The Cl2p core-level spectrum (**Fig. 3F**) with the peak component of Si2p_{3/2} at 198.30 eV suggests the existence of Cl⁻ ions as the counterion of quaternary ammonium cations on the surface of SiO₂-PDA-PDMC composites. In general, these results of XPS analysis provide further evidence for the successful coating of PDA and functionalization with PDMC.

3.2. Adsorption experiment studies

3.2.1 Effect of contact time and adsorption kinetics

The contact time plays an essential role in the adsorption process. **Fig. 4A** shows the effect of contact time on the adsorption of CR onto pure SiO_2 and SiO_2 -PDA-PDMC. As is clear from the curves, the amount of adsorbed CR was increased rapidly in initial 10 min. Soon afterwards, the incremental tendency began to weaken until the adsorption balance was reached. It may be the reason that plenty of adsorption active sites on the surface of polymer layer are available at initial stage, then the CR molecules slowly diffuse from surface of polymer onto the SiO_2 surface because those active sites on the surface of polymer layer are occupied, and finally, the adsorption reach equilibrium after almost adsorption active sites on the surface of SiO_2 spheres are occupied. The adsorption equilibrium time of SiO_2 and SiO_2 -PDA-PDMC are about 30 and 60 min, respectively. The increase of adsorption equilibrium time is attributed to the chemical adsorption between CR and cationic groups on the surface of SiO_2 -PDA-PDMC composites. According to the adsorption experimental data, the amount of adsorbed CR at equilibrium time by SiO_2 -PDA-PDMC composites is around 76.75 mg/g, while that of pure SiO_2 particles is just 28.66 mg/g. The enhancement of adsorption capacity benefits from the functionalization with cationic polymer PDMC. The cationic polymer PDMC provides countless adsorption active sites for the adsorbent. Thus, the SiO_2 -PDA-PDMC composites have better adsorption performance than pure SiO_2 particles.

Fig. 4 Effect of contact time on the adsorption capacity of CR onto pure SiO_2 and SiO_2 -PDA-PDMC (Adsorbent, 10 mg; volume, 50 mL; initial CR concentration, 50 mg/L; temperature, 299 K; time, 0-60 min) (A); Kinetic plots for adsorption of CR onto SiO_2 -PDA-PDMC composites (B).

The adsorption kinetics is of great significance for the understanding of adsorption process. In order to gain more information for comprehending the mechanism of CR adsorption, the pseudo-first-order kinetic model and pseudo-second-order were used in this study to fit the experimental data. The pseudo-first-order kinetic model is based on the assumption that the adsorption process is controlled by diffusion. The adsorption rate is proportional to the value of difference between equilibrium adsorption capacity and adsorption amount at time t [59]. The pseudo-second-order model assumes that the adsorption process is controlled by chemical adsorption involving the valence forces via the exchange or sharing electrons between adsorption active sites on the

surface of adsorbent and adsorbate [60]. The non-linear forms of pseudo-first-order (3) and pseudo-second-order (4) kinetic equations are given as follows:

$$Q_t = Q_e(1 - e^{-k_1 t}) \quad (3)$$

$$Q_t = \frac{k_2 Q_e^2 t}{1 + k_2 Q_e t} \quad (4)$$

Where Q_e (mg/g) and Q_t (mg/g) are equilibrium adsorption capacity and adsorption amount at time t (min), respectively. The k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) represent the rate constants of the pseudo-first-order and pseudo-second-order, respectively. The fitted curves of these kinetic models are shown in **Fig. 4B**. The values of these kinetic parameters and correlation coefficients (R^2) are listed in **Table 1**. As can be seen in **Table 1**, the R^2 value of pseudo-second-order model is greater than that of pseudo-first-order model. It suggests that the adsorption of CR onto SiO_2 -PDA-PDMC is better fitted by pseudo-second-order. Furthermore, the value of $Q_{e(\text{cal})}$ (mg/g) from pseudo-second-order is found to be much closer to the experimental result than that of pseudo-first-order model. This result further confirms that pseudo-second-order could well describe the kinetics of CR adsorbed onto SiO_2 -PDA-PDMC composites. According to these results, it can be concluded that the rate-limiting step in adsorption of CR is controlled by chemical adsorption.

Table 1 Adsorption kinetic parameters for the adsorption of CR onto SiO_2 -PDA-PDMC composites.

Models	Parameters	Initial concentration (mg/L)
		50
Pseudo-first-order equation	$Q_{e(\text{cal})}$ (mg/g)	66.14
	k_1 (min^{-1})	0.1720
	R^2	0.9260
Pseudo-second-order equation	$Q_{e(\text{cal})}$ (mg/g)	76.16
	k_2 ($\text{g mg}^{-1} \text{min}^{-1}$)	0.002971
	R^2	0.9726
Intraparticle diffusion	k_p ($\text{mg g}^{-1} \text{min}^{-0.5}$)	6.433
	C	30.08
	R^2	0.9704

The intraparticle diffusion model used in this study is to identifying the steps involved during the adsorption. The non-linear form of intraparticle diffusion equation (5) is expressed as:

$$Q_t = k_p t^{0.5} + C \quad (5)$$

Where k_p ($\text{mg g}^{-1} \text{min}^{-0.5}$) is the intraparticle diffusion rate constant; and C is the constant of intraparticle diffusion equation [61]. The fitted curve is shown in **Fig. 4B** and the parameters of intraparticle diffusion model are calculated and listed in **Table 1**. It is clear from the table that the experimental data have a good correlation coefficient value to intraparticle diffusion model ($R^2 > 0.9$). And the constant C is found to be more than 0. These results suggest the adsorption process also could be well described by intraparticle diffusion model and the CR adsorption process is controlled by multiple steps. Based on the above kinetic analysis, it can be inferred that the adsorption of CR onto SiO_2 -PDA-PDMC composites is both controlled by chemical adsorption and physical adsorption, and the chemical adsorption is the major rate-controlling-step.

3.2.2. Effect of initial CR concentration and adsorption isotherms

The initial CR concentration is another significant parameter on the adsorption of CR onto SiO_2 -PDA-PDMC. The effect of initial CR concentration is investigated and shown in **Fig. 5**. With increasing initial CR concentration from 25 to 300 mg/L, the adsorption capacities increased from 68.29 to 146.4 mg/g for SiO_2 -PDA-PDMC. We can observe that the rising tendency of adsorption capacity decreased with the increasing concentration and gradually achieved a balance. The reason is that the driving force from concentration gradient increased with the increasing CR concentration, but the amount of active sites is fixed. Thus, under the same condition, the high CR concentration is less able to influence the adsorption capacity with the increasing concentration.

Fig. 5 Equilibrium isotherms for adsorption of CR onto SiO_2 -PDA-PDMC composites (Adsorbent, 10 mg; volume, 50 mL; initial CR concentrations, 25-300 mg/L; temperature, 299 K; time, 60 min).

For purpose of understanding the relationship between the concentration of CR and the adsorption capacity of SiO_2 -PDA-PDMC at equilibrium, the experimental data were fitted to the Langmuir and Freundlich isotherm models. The Langmuir model is based on the hypothesis that adsorption occurs on a homogeneous surface and all the adsorbates are

independent without interaction force [62]. The Freundlich model is just an empirical equation, which is used to describe the equilibrium adsorption on the heterogeneous surface [8]. The nonlinear forms of Langmuir (6) and Freundlich (7) isotherm models are expressed as following equations, respectively:

$$Q_e = \frac{K_L Q_m C_e}{1 + K_L C_e} \quad (6)$$

$$Q_e = K_F C_e^{\frac{1}{n}} \quad (7)$$

Where K_L (L/mg) and Q_m (mg/g) are the Langmuir adsorption constants related to energy of the adsorption and adsorption capacity, respectively; K_F [(mg/g) (L/mg)^{1/n}] and n^{-1} are the Freundlich constants related to adsorption capacity and adsorption intensity, respectively. In general, the value of constant n^{-1} is between zero and one. The smaller of the value of constant n^{-1} implies the better adsorption performance. When the value of n^{-1} is beyond 2, it means the adsorption is difficult. While $n^{-1} = 1$ indicating the adsorption is homogeneous. The calculated results are listed in **Table 2** and the fitted curves are shown in **Fig. 5**.

From the data of isotherm parameters, it can be seen that the value of R^2 from Freundlich model (0.9926) is higher than that of Langmuir model (0.8385). This result indicates the adsorption of CR onto SiO₂-PDA-PDMC composites follows the Freundlich isotherm model. According to the assumption of Freundlich, the adsorption of CR occurred on a heterogeneous surface. This surface heterogeneity can be attributed to the polymer layers on the surface of SiO₂. In addition, the value of constant n^{-1} is found be 0.2417, suggesting that CR is favorably adsorbed by SiO₂-PDA-PDMC composites. Although the Langmuir isotherm model cannot well describe the adsorption process, the maximum adsorption capacity calculated from Langmuir model is found to be 142.5 mg/g. It means the SiO₂-PDA-PDMC composites can used as efficient adsorbents for the adsorption of CR from aqueous solution.

Table 2 The Langmuir and Freundlich adsorption isotherm constants and correlation coefficients.

Isotherms	Parameters	Temperatures(K)
		299
Langmuir	Q_m (mg/g)	142.50
	K_L (L/mg)	0.05250
	R_L	0.4324-0.05970
	R^2	0.8385
Freundlich	K_F [(mg/g)(L/mg) ^{1/n}]	37.17
	n^{-1}	0.2417
	R^2	0.9926

The separation factor R_L is an essential characteristic of the Langmuir isotherm [63]. In this study, it is used to evaluate the feasibility of CR adsorption on SiO₂-PDA-PDMC composites. The equation can be expressed as (8):

$$R_L = \frac{1}{1 + K_L C_0} \quad (8)$$

Where C_0 (mg/L) is the initial concentration of CR. The values of these parameters are listed in **Table 2**. In general, values of R_L in the range of 0-1 illustrates that the adsorption is favorable; $R_L = 0$ suggests the adsorption is reversible; while $R_L > 1$ implies that the adsorbate is unfavorably adsorbed on the adsorbent; $R_L = 1$ indicates that the adsorption is linear. From the calculated values of R_L , it can be known that the SiO₂-PDA-PDMC composites are favorable for the adsorption of CR under the conditions in this study.

Table 3 CR adsorption capacities Q_m of SiO₂-PDA-PDMC and other adsorbents reported in the literature

Adsorbent	Adsorption capacity (mg/g)	Experimental conditions				Refs
		Solution pH	Temperature (K)	Dosage (g/L)	CR concentration (mg/L)	
SMZ6	64.94	6	303	0.8	20-100	[64]
Saw dust	31.25	7	303	4	5-30	[65]
Reagent NiO nanoparticles	39.70	7	298	0.2	15-50	[66]
Coir pith carbon	6.72	8	308	4	20-80	[67]
Acid-treated pine cone	40.19	3.55	333	0.2	10-60	[68]
Bagasse fly ash	11.89	7	303	1.0	5-30	[69]
Banana peel	18.20	7.9	303	1.0	10-120	[70]
Hollow microspheres Ni(OH) ₂ -Si	113.60	7	303	0.2	10-100	[71]
Fe ₃ O ₄ @SiO ₂	45.46	5.3	308	0.5	30	[72]
SiO ₂ -PDA-PDMC	142.50	7	299	0.2	25-300	This work

Table 3 shows the CR adsorption capacities of the SiO₂-PDA-PDMC and some other adsorbents reported in the literature. As compared with general adsorbents in previous reports, the prepared SiO₂-PDA-PDMC composites have higher adsorption capacity of 142.50 toward CR. Although many excellent adsorbents are reported in recent years, the high adsorption capacity of SiO₂-PDA-PDMC and the simplicity of the method for preparation of SiO₂-PDA-PDMC make these particles better than the others for CR removal. And the designability of the preparation method provides technical support for the preparation of much higher adsorption efficiency adsorbents.

3.2.3. Effect of temperature and thermodynamic analyses

Temperature is also an important parameter on the adsorption process. In order to observe the effect of temperature on adsorption of CR, the batch experiments were carried out for the initial CR concentration of 50 mg/L at six different temperatures

(299, 303, 313, 323, 333 and 343 K). **Fig. 6A** shows the plots of adsorption capacity versus temperature. As is clear from **Fig. 6A**, the adsorption capacity of SiO₂-PDA-PDMC presents a significant increasing trend with the increasing temperature. This can be attributed to that the mobility of CR molecules increased with a rise of temperature. Then the adsorption active sites are occupied by more and more CR molecules. The amount of adsorbed CR increased from 78.03 to 122.8 mg/g when the temperature was raised from 299 to 343 K. These results suggest that the adsorption of CR onto SiO₂-PDA-PDMC is an endothermic process. The increase of temperature is propitious for CR to the adsorption on the surface of SiO₂-PDA-PDMC composites.

Fig. 6 Effect of temperature on the adsorption of CR onto SiO₂-PDA-PDMC composites (Adsorbent, 10 mg; volume, 50 mL; initial CR concentration, 50 mg/L; temperature, 299-343 K; time, 60 min) (A); The Van't Hoff plots for adsorption of CR onto SiO₂-PDA-PDMC composites (B).

The thermodynamic parameters, including enthalpy ΔH^0 , entropy ΔS^0 and Gibbs free energy ΔG^0 , are of great use in evaluating the effect of temperature on the adsorption of CR and can provide some meaningful information about adsorption mechanism[73]. They can be calculated using following equations (9):

$$K\alpha = \frac{Q_e}{C_e}$$

$$\Delta G^0 = -RT \ln K\alpha$$

$$\ln K\alpha = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{R \cdot T} \quad (9)$$

Where $K\alpha$ (L·g⁻¹) is the adsorption dissociation constant, which can be calculated from the ratio of equilibrium adsorption capacity Q_e (mg/g) to equilibrium concentration C_e (mg/L); T (K) represents the system temperature and R (8.314 J/mol·K) is the universal gas constant. ΔH^0 and ΔS^0 can be determined from the slope and intercept of the Van't Hoff plots of $\ln K\alpha$ versus of $1/T$ (**Fig. 6A**). ΔG^0 is calculated from the equation above. The results are listed in **Table 4**.

Table 4 Adsorption thermodynamic parameters for adsorption of CR onto SiO₂-PDA-PDMC composites at different temperatures.

T (K)	ΔG^0 (kJ·mol ⁻¹)	ΔH^0 (kJ·mol ⁻¹)	ΔS^0 (kJ·mol ⁻¹ ·K ⁻¹)
299	-1.874	11.31	0.0445
303	-2.352		
313	-2.580		
323	-3.093		
333	-3.414		
343	-4.012		

The values of ΔG^0 are found to be negative at temperature range from 299 to 343 K, indicating the adsorption of CR onto SiO₂-PDA-PDMC composites is spontaneous and thermodynamically favorable. Besides, it can be observed that the value of ΔG^0 decreased from -1.874 to -4.012 kJ·mol⁻¹ when the temperature increased from 299 to 343 K. It suggests the adsorption of CR by SiO₂-PDA-PDMC is more spontaneous at higher temperature. The positive value of ΔH^0 demonstrates that the adsorption process of CR is endothermic, which is consistent with the previous conclusion. The positive value of ΔS^0 means that the degrees of freedom of molecular motion increase with the increasing temperature at the adsorbent-adsorbate interface. According to the thermodynamic analysis, it can be known that the CR adsorption onto SiO₂-PDA-PDMC composites is favorable and the SiO₂-PDA-PDMC composites can be used as promising adsorbents for the adsorption of CR from aqueous solution.

3.2.4. Effect of solution pH on CR adsorption

To further understand the adsorption mechanism, the effect of solution pH on adsorption capacity was investigated over a range of pH values from 6 to 10 at room temperature. The experiments for CR adsorption were only performed in the pH range of 6-10 for avoiding the influence of dramatic colour change under strong acidic condition. It can be seen from **Fig. 7A** that the adsorption capacity of SiO₂-PDA-PDMC sharply decreased from 99.67 mg/g to 37.48 mg/g with the solution pH increased from 6 to 10. This result can be explained as follows: most of quaternary ammonium groups on the surface of SiO₂-PDA-PDMC are ionized at acidic solution and interacted with the CR molecules via the strong electrostatic interaction, which is favorable for the adsorption of CR onto SiO₂-PDA-PDMC. When in more basic condition, the deionization of quaternary ammonium groups is very strong and the number of ionized surface sites on the adsorbent decreased with the increasing pH, leading to the decrease of adsorption capacity of SiO₂-PDA-PDMC toward CR. It can also be confirmed from the data on the zeta potential (**Fig. 7B**). From the following figure, it is clear to see that with the change in pH there is remarkable change in zeta potential. The decrease of zeta potential was found with the increasing solution pH due to the neutralization of surface charges of the adsorbents. With increasing

solution pH, the particles of adsorbents are inclined to acquire more negative charges and deionization of quaternary ammonium groups on the surface SiO₂-PDA-PDMC becomes stronger, leading to more negative zeta potentials values of SiO₂-PDA-PDMC. In addition, the curve of zeta potential is found to be similar to the curve of adsorption capacity versus solution pH and the values of zeta potential are similar to those in literature [74]. Therefore, the fact that anionic dye CR adsorbed on SiO₂-PDA-PDMC decreased with solution pH reveals that one of the contributions of the SiO₂-PDA-PDMC adsorption toward CR resulted from the electrostatic interaction between the negatively charged CR molecules and the positively charged SiO₂-PDA-PDMC adsorbent surface.

Fig. 7 Effect of solution pH on the adsorption of CR onto SiO₂-PDA-PDMC composites (Adsorbent, 10 mg; volume, 50 mL; initial CR concentration, 50 mg/L; temperature, 299 K; time, 60 min) (A); Zeta potential versus solution pH curve obtained from SiO₂-PDA-PDMC composites (B).

4. Conclusion

In summary, the SiO₂-PDA-PDMC composites were prepared via mussel inspired chemistry and SI-ATRP. Compared to pure SiO₂ particles, the spheroidal structure of SiO₂-PDA-PDMC composites was not changed. The FT-IR, TGA data and XPS analysis provide sufficient evidence for the successful preparation of SiO₂-PDA-PDMC composites. The obtained SiO₂-PDA-PDMC composites were used as adsorbents to remove organic dyes and showed a good performance for the removal of CR from aqueous solution. The adsorption kinetics, isotherms and thermodynamics were investigated in batch adsorption experiments. The adsorption results showed that adsorption of CR onto SiO₂-PDA-PDMC was a fast and efficient process. The CR adsorption equilibrium was achieved within 60 min. The adsorption capacity of SiO₂-PDA-PDMC was higher than that of pure SiO₂. The kinetics study revealed that the adsorption of CR onto SiO₂-PDA-PDMC followed the pseudo-second-order model. The isotherm data indicated that the Freundlich isotherm model was more appropriate to fit the adsorption data. The thermodynamic analysis demonstrated that the adsorption process of CR is spontaneous and endothermic in nature. The anionic dye CR adsorbed on SiO₂-PDA-PDMC decreased with pH due to the electrostatic interaction between the negatively charged CR molecules and the positively charged SiO₂-PDA-PDMC adsorbent surface. This work shows that integration of cationic polymers and SiO₂ could

improve the adsorption efficiency and the SiO₂-PDA-PDMC composites could be considered as promising adsorbents for the anionic dyes removal from aqueous solution.

Acknowledgments

This research was supported by the National Science Foundation of China (Nos. 51363016, 21474057, 21564006, 21561022, 21644014), Natural Science Foundation of Jiangxi Province in China (Nos. 20161BAB203072, 20161BAB213066) and the National 973 Project (Nos. 2011CB935700).

References

- [1] J.W. Fu, Z.H. Chen, M.H. Wang, S.J. Liu, J.H. Zhang, J.N. Zhang, R.P. Han, Q. Xu, Adsorption of methylene blue by a high-efficiency adsorbent (polydopamine microspheres): Kinetics, isotherm, thermodynamics and mechanism analysis, *Chemical Engineering Journal*, 259 (2015) 53-61.
- [2] M. Vakili, M. Rafatullah, B. Salamatinia, A.Z. Abdullah, M.H. Ibrahim, K.B. Tan, Z. Gholami, P. Amouzgar, Application of chitosan and its derivatives as adsorbents for dye removal from water and wastewater: A review, *Carbohydrate polymers*, 113 (2014) 115-130.
- [3] A. Middea, L.S. Spinelli, F.G. Souza, R. Neumann, O. da FM Gomes, T.L. Fernandes, L.C. de Lima, V.M. Barthém, F.V. de Carvalho, Synthesis and characterization of magnetic palygorskite nanoparticles and their application on methylene blue remotion from water, *Appl. Surf. Sci.*, 346 (2015) 232-239.
- [4] J. Varghese, K. Varghese, Graphene/CuS/ZnO hybrid nanocomposites for high performance photocatalytic applications, *Mater. Chem. Phys.*, 167 (2015) 258-264.
- [5] E.A.N. Simonetti, L. de Simone Cividanes, T.M.B. Campos, B.R.C. de Menezes, F.S. Brito, G.P. Thim, Carbon and TiO₂ synergistic effect on methylene blue adsorption, *Mater. Chem. Phys.*, 177 (2016) 330-338.
- [6] M. Sheibani, M. Ghaedi, F. Marahel, A. Ansari, Congo red removal using oxidized multiwalled carbon nanotubes: kinetic and isotherm study, *Desalin Water Treat*, 53 (2015) 844-852.
- [7] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes Pigments*, 54 (2002) 47-58.
- [8] L. Wang, J. Li, Y. Wang, L. Zhao, Q. Jiang, Adsorption capability for Congo red on nanocrystalline MFe₂O₄ (M= Mn, Fe, Co, Ni) spinel ferrites, *Chem Eng J*, 181 (2012) 72-79.
- [9] A. Afkhami, R. Moosavi, Adsorptive removal of Congo red, a carcinogenic textile dye, from aqueous solutions by maghemite nanoparticles, *J Hazard Mater*, 174 (2010) 398-403.
- [10] V. Vimonses, S. Lei, B. Jin, C.W. Chow, C. Saint, Kinetic study and equilibrium isotherm analysis of Congo Red adsorption by clay materials, *Chem Eng J*, 148 (2009) 354-364.
- [11] M. Riera-Torres, C. Gutiérrez-Bouzán, M. Crespi, Combination of coagulation–flocculation and nanofiltration techniques for dye removal and water reuse in textile effluents, *Desalination*, 252 (2010) 53-59.
- [12] J.-H. Huang, C.-F. Zhou, G.-M. Zeng, X. Li, J. Niu, H.-J. Huang, L.-J. Shi, S.-B. He, Micellar-enhanced ultrafiltration of methylene blue from dye wastewater via a polysulfone hollow fiber membrane, *J Membrane Sci*, 365 (2010) 138-144.
- [13] P. Malik, S. Saha, Oxidation of direct dyes with hydrogen peroxide using ferrous ion as catalyst, *Sep Purif Technol*, 31 (2003) 241-250.
- [14] X. Liu, T. Zhao, H. Cheng, C. Zhu, S. Li, P. Cui, In-situ synthesis of nanomagnetites on poly (amidoamine)-modified graphite oxides and their novel catalytic performances towards the degradation of p-nitroaniline, *Appl. Surf. Sci.*, 327 (2015) 226-232.
- [15] L. Ma, W. Xu, S. Zhu, Z. Cui, X. Yang, A. Inoue, Anatase TiO₂ hierarchical nanospheres with enhanced photocatalytic activity for degrading methyl orange, *Mater. Chem. Phys.*, 170 (2016) 186-192.
- [16] S. Zhang, D. Wang, L. Song, A novel F-doped BiOCl photocatalyst with enhanced photocatalytic performance, *Mater. Chem. Phys.*, 173 (2016) 298-308.
- [17] C.-Y. Wu, K.-J. Tu, Y.-S. Lo, Y.L. Pang, C.-H. Wu, Alkaline hydrogen peroxide treatment for TiO₂ nanoparticles with superior water-dispersibility and visible-light photocatalytic activity, *Mater. Chem. Phys.*, 181 (2016) 82-89.

- [18] X. Wang, H. Hu, S. Chen, K. Zhang, J. Zhang, W. Zou, R. Wang, One-step fabrication of BiOCl/CuS heterojunction photocatalysts with enhanced visible-light responsive activity, *Mater. Chem. Phys.*, 158 (2015) 67-73.
- [19] Y. Lu, Y. Wan, S. Bi, H. Weng, Y. Huang, L. Qin, H.J. Seo, Synthesis, surface and optical properties of Ag₂CaV₄O₁₂ nanoparticles for dye removal under visible irradiation, *Mater. Chem. Phys.*, (2016).
- [20] C.G. Anchietia, E.C. Severo, C. Rigo, M.A. Mazutti, R.C. Kuhn, E.I. Muller, E.M. Flores, R.F. Moreira, E.L. Foletto, Rapid and facile preparation of zinc ferrite (ZnFe₂O₄) oxide by microwave-solvothermal technique and its catalytic activity in heterogeneous photo-Fenton reaction, *Mater. Chem. Phys.*, 160 (2015) 141-147.
- [21] M. Purkait, S. DasGupta, S. De, Removal of dye from wastewater using micellar-enhanced ultrafiltration and recovery of surfactant, *Sep Purif Technol*, 37 (2004) 81-92.
- [22] Q. Huang, M. Liu, J. Chen, K. Wang, D. Xu, F. Deng, H. Huang, X. Zhang, Y. Wei, Enhanced removal capability of kaolin toward methylene blue by mussel-inspired functionalization, *J Mater Sci*, (2016) 1-15.
- [23] Y. Meng, D. Chen, Y. Sun, D. Jiao, D. Zeng, Z. Liu, Adsorption of Cu²⁺ ions using chitosan-modified magnetic Mn ferrite nanoparticles synthesized by microwave-assisted hydrothermal method, *Appl. Surf. Sci.*, 324 (2015) 745-750.
- [24] P. Wang, M. Cao, C. Wang, Y. Ao, J. Hou, J. Qian, Kinetics and thermodynamics of adsorption of methylene blue by a magnetic graphene-carbon nanotube composite, *Appl. Surf. Sci.*, 290 (2014) 116-124.
- [25] B. Yu, X. Zhang, J. Xie, R. Wu, X. Liu, H. Li, F. Chen, H. Yang, Z. Ming, S.-T. Yang, Magnetic graphene sponge for the removal of methylene blue, *Appl. Surf. Sci.*, 351 (2015) 765-771.
- [26] X. Zhang, Q. Huang, M. Liu, J. Tian, G. Zeng, Z. Li, K. Wang, Q. Zhang, Q. Wan, F. Deng, Preparation of amine functionalized carbon nanotubes via a bioinspired strategy and their application in Cu²⁺ removal, *Appl. Surf. Sci.*, 343 (2015) 19-27.
- [27] K.P. Gopinath, S. Murugesan, J. Abraham, K. Muthukumar, Bacillus sp. mutant for improved biodegradation of Congo red: random mutagenesis approach, *Bioresource technology*, 100 (2009) 6295-6300.
- [28] B. Erdem, M. Erdem, A.S. Ozcan, Adsorption of Reactive Black 5 onto quaternized 2-dimethylaminoethyl methacrylate based polymer/clay nanocomposites, *Adsorption-Journal Of the International Adsorption Society*, 22 (2016) 767-776.
- [29] J. Liu, S. Ma, L. Zang, Preparation and characterization of ammonium-functionalized silica nanoparticle as a new adsorbent to remove methyl orange from aqueous solution, *Appl Surf Sci*, 265 (2013) 393-398.
- [30] C.N. Heng, M.Y. Liu, K. Wang, F.J. Deng, H.Y. Huang, Q. Wan, J.F. Hui, X.Y. Zhang, Y. Wei, Biomimic preparation of highly dispersible silica nanoparticles based polymer nanocomposites, *Ceramics International*, 41 (2015) 15075-15082.
- [31] Q. Huang, M. Liu, F. Deng, K. Wang, H. Huang, D. Xu, G. Zeng, X. Zhang, Y. Wei, Mussel inspired preparation of amine-functionalized Kaolin for effective removal of heavy metal ions, *Mater. Chem. Phys.*, 181 (2016) 116-125.
- [32] Z. Yang, H. Li, H. Yan, H. Wu, H. Yang, Q. Wu, H. Li, A. Li, R. Cheng, Evaluation of a novel chitosan-based flocculant with high flocculation performance, low toxicity and good floc properties, *J Hazard Mater*, 276 (2014) 480-488.
- [33] W. Wang, J. Tang, Z. Jia, X. Li, Z. Xiao, Grafting of amphiphilic polymers containing quaternary ammonium group on SiO₂ surface via surface-initiated ATRP, *J Polym Res*, 19 (2012) 1-8.
- [34] Z. Jia, W. Yuan, H. Zhao, H. Hu, G.L. Baker, Composite electrolytes comprised of poly (ethylene oxide) and silica nanoparticles with grafted poly (ethylene oxide)-containing polymers, *RSC Adv*, 4 (2014) 41087-41098.
- [35] K. Ohno, T. Morinaga, K. Koh, Y. Tsujii, T. Fukuda, Synthesis of monodisperse silica particles coated with well-defined, high-density polymer brushes by surface-initiated atom transfer radical polymerization, *Macromolecules*, 38 (2005) 2137-2142.
- [36] J.H. Waite, T.J. Housley, M.L. Tanzer, Peptide repeats in a mussel glue protein: theme and variations, *Biochemistry*, 24 (1985) 5010-5014.
- [37] J. Tian, H. Zhang, M. Liu, F. Deng, H. Huang, Q. Wan, Z. Li, K. Wang, X. He, X. Zhang, A bioinspired strategy for surface modification of silica nanoparticles, *Appl. Surf. Sci.*, 357 (2015) 1996-2003.
- [38] Q. Wan, J. Tian, M. Liu, G. Zeng, Q. Huang, K. Wang, Q. Zhang, F. Deng, X. Zhang, Y. Wei, Surface modification of carbon nanotubes via combination of mussel inspired chemistry and chain transfer free radical polymerization, *Appl. Surf. Sci.*, 346 (2015) 335-341.
- [39] Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Y. Wei, Mussel-inspired chemistry and Michael addition reaction for efficient oil/water separation, *ACS Appl Mater Inter*, 5 (2013) 4438-4442.

- [40] P. Gao, M. Liu, J. Tian, F. Deng, K. Wang, D. Xu, L. Liu, X. Zhang, Y. Wei, Improving the drug delivery characteristics of graphene oxide based polymer nanocomposites through the “one-pot” synthetic approach of single-electron-transfer living radical polymerization, *Appl Surf Sci*, 378 (2016) 22-29.
- [41] Q. Wan, J.W. Tian, M.Y. Liu, G.J. Zeng, Q. Huang, K. Wang, Q.S. Zhang, F.J. Deng, X.Y. Zhang, Y. Wei, Surface modification of carbon nanotubes via combination of mussel inspired chemistry and chain transfer free radical polymerization, *Applied Surface Science*, 346 (2015) 335-341.
- [42] Y. Cao, X. Zhang, L. Tao, K. Li, Z. Xue, L. Feng, Y. Wei, Mussel-inspired Chemistry and Michael addition Reaction for Efficient Oil/water Separation, *ACS Appl. Mater. Interf.*, 5 (2013) 4438–4442.
- [43] H. Gao, Y. Sun, J. Zhou, R. Xu, H. Duan, Mussel-inspired synthesis of polydopamine-functionalized graphene hydrogel as reusable adsorbents for water purification, *ACS Appl Mater Inter*, 5 (2013) 425-432.
- [44] M.H. Ryou, Y.M. Lee, J.K. Park, J.W. Choi, Mussel - Inspired Polydopamine - Treated Polyethylene Separators for High - Power Li - Ion Batteries, *Adv Mater*, 23 (2011) 3066-3070.
- [45] W. Sheng, B. Li, X. Wang, B. Dai, B. Yu, X. Jia, F. Zhou, Brushing up from "anywhere" under sunlight: a universal surface-initiated polymerization from polydopamine-coated surfaces, *Chem. Sci.*, 6 (2015) 2068-2073.
- [46] Q. Huang, M. Liu, J. Chen, K. Wang, D. Xu, F. Deng, H. Huang, X. Zhang, Y. Wei, Mussel inspired preparation of functional silica nanocomposites for environmental adsorption applications, *Appl Surf Sci*, 387 (2016) 285-293.
- [47] C. Heng, M. Liu, K. Wang, X. Zheng, H. Huang, F. Deng, J. Hui, X. Zhang, Y. Wei, Fabrication of silica nanoparticle based polymer nanocomposites via a combination of mussel inspired chemistry and SET-LRP, *RSC Advances*, 5 (2015) 91308-91314.
- [48] R.M. Bielecki, P. Doll, N.D. Spencer, Ultrathin, oil-compatible, lubricious polymer coatings: A comparison of grafting-to and grafting-from strategies, *Tribology Letters*, 49 (2013) 273-280.
- [49] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-inspired surface chemistry for multifunctional coatings, *Science*, 318 (2007) 426-430.
- [50] O. Pop-Georgievski, C. Rodriguez-Emmenegger, A.D. Pereira, V. Proks, E. Brynda, F. Rypacek, Biomimetic non-fouling surfaces: extending the concepts, *Journal Of Materials Chemistry B*, 1 (2013) 2859-2867.
- [51] P. Król, P. Chmielarz, Recent advances in ATRP methods in relation to the synthesis of copolymer coating materials, *Progress in Organic Coatings*, 77 (2014) 913-948.
- [52] Z. Ma, X. Jia, J. Hu, Z. Liu, H. Wang, F. Zhou, Mussel-Inspired Thermosensitive Polydopamine-graft-Poly (N-isopropylacrylamide) Coating for Controlled-Release Fertilizer, *Journal of agricultural and food chemistry*, 61 (2013) 12232-12237.
- [53] L.M. Wu, D.S. Tong, L.Z. Zhao, W.H. Yu, C.H. Zhou, H. Wang, Fourier transform infrared spectroscopy analysis for hydrothermal transformation of microcrystalline cellulose on montmorillonite, *Appl Clay Sci*, 95 (2014) 74-82.
- [54] X.Z. Zhang, Y. Huang, K.Q. Fu, S.J. Yuan, C. Huang, H.B. Li, Preparation and performance of cationic flocculant for papermaking based on the graft polymerization of cationic chains from colloidal silica particles, *Colloids And Surfaces a-Physicochemical And Engineering Aspects*, 491 (2016) 29-36.
- [55] W.J. Yang, K.-G. Neoh, E.-T. Kang, S.L.-M. Teo, D. Rittschof, Stainless steel surfaces with thiol-terminated hyperbranched polymers for functionalization via thiol-based chemistry, *Polymer Chemistry*, 4 (2013) 3105-3115.
- [56] Z.-Y. Xi, Y.-Y. Xu, L.-P. Zhu, Y. Wang, B.-K. Zhu, A facile method of surface modification for hydrophobic polymer membranes based on the adhesive behavior of poly (DOPA) and poly (dopamine), *Journal of Membrane Science*, 327 (2009) 244-253.
- [57] S. Yang, L. Liu, Z. Jia, W. Fu, D. Jia, Y. Luo, Study on the structure-properties relationship of natural rubber/SiO₂ composites modified by a novel multi-functional rubber agent, *Express Polym Lett*, 8 (2014) 425-435.
- [58] C. Tang, J. Zhu, Q. Zhou, J. Wei, R. Zhu, H. He, Surface heterogeneity of SiO₂ polymorphs: an XPS investigation of α -quartz and α -cristobalite, *The Journal of Physical Chemistry C*, 118 (2014) 26249-26257.
- [59] Q. Huang, M. Liu, J. Chen, K. Wang, D. Xu, F. Deng, H. Huang, X. Zhang, Y. Wei, Enhanced removal capability of kaolin toward methylene blue by mussel-inspired functionalization, *J Mater Sci*, 1-15.
- [60] I.A. Darwish, D.A. Blake, Development and validation of a one-step immunoassay for determination of cadmium in human serum, *Anal Chem*, 74 (2002) 52-58.

- [61] P.F. Sun, C. Hui, R.A. Khan, J.T. Du, Q.C. Zhang, Y.H. Zhao, Efficient removal of crystal violet using Fe₃O₄-coated biochar: the role of the Fe₃O₄ nanoparticles and modeling study their adsorption behavior, *Scientific Reports*, 5 (2015).
- [62] S.M. Rafigh, A.V. Yazdi, A.A. Safekordi, A.H. Nasab, M. Ardjmand, F. Naderi, H. Mozafari, Protein adsorption using novel carboxymethyl-curdlan microspheres, *Int Biol Macromol*, 87 (2016) 603-610.
- [63] A. Dada, A. Olalekan, A. Olatunya, O. Dada, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ unto phosphoric acid modified rice husk, *RUSS J Appl Chem*, 3 (2012) 38-45.
- [64] S. Liu, Y. Ding, P. Li, K. Diao, X. Tan, F. Lei, Y. Zhan, Q. Li, B. Huang, Z. Huang, Adsorption of the anionic dye Congo red from aqueous solution onto natural zeolites modified with N, N-dimethyl dehydroabietylamine oxide, *Chemical Engineering Journal*, 248 (2014) 135-144.
- [65] V.S. Mane, P.V. Babu, Kinetic and equilibrium studies on the removal of Congo red from aqueous solution using Eucalyptus wood (*Eucalyptus globulus*) saw dust, *Journal of the Taiwan Institute of Chemical Engineers*, 44 (2013) 81-88.
- [66] B. Cheng, Y. Le, W. Cai, J. Yu, Synthesis of hierarchical Ni (OH)₂ and NiO nanosheets and their adsorption kinetics and isotherms to Congo red in water, *Journal of Hazardous Materials*, 185 (2011) 889-897.
- [67] C. Namasivayam, D. Kavitha, Removal of Congo Red from water by adsorption onto activated carbon prepared from coir pith, an agricultural solid waste, *Dyes and pigments*, 54 (2002) 47-58.
- [68] S. Dawood, T.K. Sen, Removal of anionic dye Congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design, *Water research*, 46 (2012) 1933-1946.
- [69] I.D. Mall, V.C. Srivastava, N.K. Agarwal, I.M. Mishra, Removal of congo red from aqueous solution by bagasse fly ash and activated carbon: kinetic study and equilibrium isotherm analyses, *Chemosphere*, 61 (2005) 492-501.
- [70] G. Annadurai, R.-S. Juang, D.-J. Lee, Use of cellulose-based wastes for adsorption of dyes from aqueous solutions, *Journal of hazardous materials*, 92 (2002) 263-274.
- [71] C. Lei, X. Zhu, B. Zhu, J. Yu, W. Ho, Hierarchical NiO–SiO₂ composite hollow microspheres with enhanced adsorption affinity towards Congo red in water, *Journal of colloid and interface science*, 466 (2016) 238-246.
- [72] P. Wang, X. Wang, S. Yu, Y. Zou, J. Wang, Z. Chen, N.S. Alharbi, A. Alsaedi, T. Hayat, Y. Chen, Silica coated Fe₃O₄ magnetic nanospheres for high removal of organic pollutants from wastewater, *Chemical Engineering Journal*, 306 (2016) 280-288.
- [73] H.-Y. Zhu, Y.-Q. Fu, R. Jiang, J.-H. Jiang, L. Xiao, G.-M. Zeng, S.-L. Zhao, Y. Wang, Adsorption removal of congo red onto magnetic cellulose/Fe₃O₄/activated carbon composite: equilibrium, kinetic and thermodynamic studies, *Chem Eng J*, 173 (2011) 494-502.
- [74] X. Li, T. Yang, Q. Gao, J. Yuan, S. Cheng, Biomimetic synthesis of copolymer–silica nanoparticles with tunable compositions and surface property, *Journal of colloid and interface science*, 338 (2009) 99-104.

Cationic polymers functionalized silica nanocomposites have been fabricated through the combination of mussel inspired surface initiated atom transfer radical polymerization and utilized for removal of Congo red