One-pot solvothermal synthesis of Carboxylatopillar[5]arene-modified Fe₃O₄ magnetic nanoparticles for ultrafast separation of cationic dyes

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ABSTRACT

Carboxylatopillar[5]arene-modified Fe₃O₄ magnetic nanoparticles (CP5-MNPs), with highly controllable particle size distribution, are successfully prepared through a newly developed one-pot solvothermal strategy for the first time. Due to the strong supramolecular host-guest interactions in conjunction with appreciable magnetic responsiveness, CP5-MNPs show excellent adsorption performance and ultrafast adsorption efficiency in the separation and enrichment of organic cationic dyes, including but not limited to methylene blue and crystal violet. Significantly, the excellent dye separation performance of CP5-MNPs demonstrates a strong tolerance towards pH changes and a good resistance to inorganic salts interference. The materials’ inherent features of easy recyclability and affordability endow them with great potentials in column adsorption filler for sewage regeneration and environmental purification.

1. Introduction

Organic pollutants represent an acute threat to human health and ecological equilibrium. Particular attention has been paid to organic dye pollutants, a safety concern associated with the rapid development of textile and dyestuff industries [1,2]. They always exhibit serious environmental disruption due to its massive emission, non-biodegradable and unbounded diffusion [3,4], suggesting the great importance of its reasonable separation and recycle. Thus, design and development of dyes treatment materials/technologies are always one of the cutting-edge research projects in green chemistry and materials science [5–7]. Among them, chemical coagulation, electrochemical coagulation, advanced oxidation process, membrane technology, and photolysis and adsorption are most persuasive examples and have been widely applied [8–13]. However, in spite of many advancements in traditional adsorption treatment methods, many limitations still exist, such as low efficiency, high-cost budget and non-recyclability [14–17]. Therefore, developing new adsorption materials for high performance organic dyestuff separations are still in urgent need, not only for fundamental research but also for practical applications [18–20].

On the other hand, magnetic nanoparticles (MNPs), emerged as a powerful class of ideal adsorbents, have been given broad attention due to its low cost, good controllability, nontoxicity, and more importantly, the capability of magnetic responsiveness that ensures its recycle and reuse [21–23]. Meanwhile, its surface modification with different kinds of functional groups is a considerable method to enhance its performance and thus extend its applications [24–27]. Pillar[n]arenes (pillarenes) and derivatives are a relatively new class of supramolecular macrocyclic receptors [28–32], and the binding of carboxylato-pillar[5,6]arenes with dyes or organic pollutants have been extensively studied and tested [33–37]. Therefore, it is of great importance to develop pillararene-decorated magnetic nanoparticles for effluent disposal, taking both advantages of pillararene and magnetic nanoparticles as aforementioned.

Herein, we introduce such an example, a new method to construct carboxylatopillar[5]arene (CP5)-modified Fe₃O₄ magnetic nanoparticles (CP5-MNPs), and investigate their adsorption performance in the separation of cationic dyes (Fig. 1).
2. Results and discussion

Aiming at easy preparation, a distinct, facile one-pot solvothermal strategy was employed. In a heating process (473 K), ferric iron (FeCl₃·6H₂O) was reduced to a form of magnetic nanocrystals (Fe₃O₄ nanoparticles), which were covered as well as prevented from aggregation by CP5 macrocycles [38–40]. We envisioned that the particle size of CP5-MNPs might be highly controllable by the mole ratios of CP5 and FeCl₃·6H₂O. As expected, a series of control experiments with different dosage of CP5 macrocycles rendered a wide range of nanoparticle sizes from 147 ± 17 nm to 446 ± 57 nm (Fig. 2), strongly confirming the role of CP5 in the regulation of particle diameter. Experiments by altering the reaction temperature (varied from 473 K to 503 K, Fig. S4, ESI) and reaction time (varied from 6 h to 12 h, Fig. S5, ESI) were also carried out, which exhibited little influence on the particle size distribution. Compared with the multi-step preparation methods on macrocycle post-modified Fe₃O₄ nanoparticles previous reported by us and others [41–44], this newly developed one-step strategy is more straightforward and convenient, which will also benefit the mass production of this new functional magnetic nanomaterials.

Fourier transform infrared (FT-IR) spectrum of CP5-MNPs shows a characteristic absorption band at 609 cm⁻¹ (Fig. 3a) that corresponds to the Fe—O stretching, indicating the formation of iron oxide compound. Meanwhile, the C=O bands of CP5 at 1606 cm⁻¹ and...
1423 cm$^{-1}$ are resulted from the successful coating of CP5 macrocycles on MNP surface. Furthermore, powder X-ray diffraction (PXRD) pattern of CP5-MNPs (Fig. 3b) confirms the formation of the desired crystal structure, and the peaks of (220), (311), (400), (511) and (440) are in a good agreement with the face-centered cubic structures of Fe$_3$O$_4$ (JCPDS 75-1609) [45–47]. In addition, X-ray photoelectron spectrum (XPS) was employed, and two representative peaks (711.4 and 724.6 eV, Fig. 3c) suggest that the Fe 2p$_{3/2}$ and Fe 2p$_{1/2}$ do exist in the CP5-MNPs [48–50]. The characteristic peaks of CP5, corresponding to the oxygen and carbon atoms, have also been observed (Fig. S6, ESI).

Preeminent magnetic response properties are always desirable and valuable for magnetic adsorption materials [51,52]. According to the magnetic measurement (Fig. 3d), the saturation magnetization of CP5-MNPs with a particle diameter of 446 ± 57 nm is 51 emu g$^{-1}$ without any coercivity or remanence. More intuitively, the photograph presents a clear dispersion and aggregation of CP5-MNPs in response to an external magnetic field (Fig. 3d).

Two representative cationic organic dyes, e.g., methylene blue (MB) and crystal violet (CV), were selected to evaluate the adsorption performance of CP5-MNPs. Solution adsorption experiments by CP5-MNPs of different diameters were carried out. As shown in Fig. S9 (ESI), the removal efficiency renders a decrease of particle size from 446 ± 57 nm to 147 ± 17 nm, suggesting that the CP5 macrocycles modified on the surface of Fe$_3$O$_4$ nanoparticles play a dominant role, as verified by subsequent thermogravimetric analysis (Fig. S10 and Table S1, ESI). The CP5-MNPs with an average diameter of 446 ± 57 nm possess the best dye removal efficiency, which was chosen for the following adsorption experiments. The final removal efficiencies of dyes by CP5-MNPs with a diameter of 446 ± 57 nm were determined by UV–Vis spectroscopy experiment. As in Fig. 4 and Fig. S11 (ESI), almost entire MB and CV dyes were efficiently removed (98.6% and 98.9%, respectively). In addition, another common cationic organic pollutant-dimethyl viologen salt (MV) could also be highly efficiently adsorbed (97.3% adsorption efficiency, Fig. S21, ESI), suggesting a good pollutant species tolerance of CP5-MNPs nanomaterial. Significantly, CP5-MNPs displayed an excellent performance stability in a wide range of solution pH values. As shown in Fig. S12a (ESI), the dyes removal efficiencies were almost invariable with the pH values ranging from 3 to 10. However, under extremely acidic conditions, the decorative anionic CP5 macrocycles are protonated, which greatly weakened its binding properties as well as performance due to the diminution of electrostatic interactions [53,54]. Significantly, CP5-MNPs presented an excellent capability in resisting the disturbance of common inorganic salts (Fig. S12b and Fig. S13, ESI). Overall, we further demonstrated that these newly formed CP5-coated Fe$_3$O$_4$ nanoparticles still capture dyes without decreased performance in a slightly complex water environment.

In addition, according to the measuring method already reported (ESI), the dye adsorption isotherm of the CP5-MNPs was obtained, more in line with the Langmuir model (Fig. S14, Table S2, ESI), suggesting a monolayer adsorption pattern [55]. What’s more, the kinetic characteristics of the adsorption process were systematically studied. UV–Vis experiments confirmed that the dyes removal efficiency was up to 90% after only less than 5 min continuous solution adsorption, and took about a further 30 min to reach the equilibrium adsorption (Fig. S15, ESI). The adsorption rate equations tailored with the pseudo-second-order kinetic model (Fig. S16, ESI), which presented a faster adsorption rate than most of the magnetic adsorbents reported (Table S5, ESI). Compared with other magnetic adsorbents, the adsorption capacity of CP5-MNPs is medium to good, whose maximum capacities for MB and CV are 136.29 and 140.26 mg g$^{-1}$, respectively (Table S3, ESI). Significantly, the adsorbed CP5-MNPs could, indeed, be easily regenerated via elution of the adsorbed nanoparticles by ethanol solution containing 5 vol% acetic acid at ambient temperature. Over 95% removal efficiency still retained after consecutive regeneration in five cycles (Fig. S20, ESI).

In order to explore the adsorption mechanism, the binding properties of CP5 with MB and CV were investigated by $^1$H NMR spectroscopy using 1:1 host-guest mixtures (Fig. S17-S18, ESI). Compared with those of free dyes, characteristic protons of dyes in the presence of CP5 obviously shifted upfield, as a consequence of host-guest interactions. In the meantime, to further explain the mechanism, another important Fe$_3$O$_4$ nanoparticle decorated with the monomer of CP5, i.e., sodium 2,2’-(1,4-phenylene(oxy))diacetate, was successfully prepared via
the same one-pot method (ESI). No effective π-donor cavities exist on the surface of Fe₃O₄ nanoparticles, thus unsurprisingly, scarcely any dyes were adsorbed (Fig. S19, ESI), giving a much more convincing evidence for the necessity of supramolecular host-guest interactions of macrocyclic hosts in dye capture.

Ultrafast adsorption performance makes CP5-MNPs an effective adsorption filling material. To visualize this, a syringe with two filled filters (4 mg of CP5-MNPs placed in) was made to simulate the real adsorption column (Fig. 1). It can be clearly seen that the MB/CV solutions turned completely colorless after passing through the adsorption device. A UV–Vis measurement showed that the dye concentration was decreased to extremely low (Fig. 4). However, in sharp contrast, the filters without CP5-MNPs packed in exhibited no adsorption capability toward the cationic dyes.

3. Conclusions

In conclusion, we presented a new type of pillarene-functionalized Fe₃O₄ nanoparticles, i.e., CP5-MNPs, through a completely new one-pot solvothermal method. CP5-MNPs performed extremely well in the capture of cationic dyes, and this new material showed high stability and excellent adsorption performance no matter in a wide fluctuation in pH (from 3 to 10) or upon facing interference of high concentration inorganic salts. In addition, its regeneration is simple, where only washing is necessary, and it can be recycled many times with no obvious decrease in performance. Overall, the ultrafast adsorption efficiency, as well as the extremely good recyclability, renewability, durability, and affordability of CP5-MNPs suggest a steady potential application of this type of new functional materials in sewage-treatment devices such as adsorbing column. We envision that these new magnetic materials can excel in a wide range of applications, not only in fundamental scientific research, but also in potentially solving real environmental problems.

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Appendix B. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.dyepig.2018.10.061.

References
