Electronic Supplementary Information (ESI) for RSC Advances
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Electronic Supplementary Information

Simultaneously capture methyl orange and chromium (VI) from complex wastewater using polyethylenimine cation decorated magnetic carbon nanotubes as a recyclable adsorbent

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1. Experimental details

1.1. Adsorption experiments in mono-pollutant system

1.1.1. Effect of solution pH on adsorption of MO and Cr(VI)

To evaluate the effect of pH on adsorption, 3 mg of MWCNTs@Fe_3O_4/PEI adsorbent was added to 30 mL of adsorbate solution with concentration of 200 mg L^{-1} for MO and 50 mg L^{-1} for Cr(VI). After adjusting solution pH in the range of 2 to 11 using diluted HCl or NaOH, the mixture was continuously shaken in a thermostatic shaker at 25°C to reach equilibrium. The liquid/solid phase separation was quickly achieved by a permanent magnet and the residual concentration of MO and Cr(VI) in the supernatant was measured by UV-vis absorption spectroscopy (UV-754N Shanghai, China).

1.1.2. Adsorption kinetics

The adsorption kinetics of MO on three different adsorbents (MWCNTs, MWCNTs@Fe_3O_4, MWCNTs@Fe_3O_4/PEI) was performed by mixing 3 mg of adsorbent with 30 mL of MO solution at constant pH value of 3 (with initial concentration of 200 mg L^{-1}). While for Cr(VI), 10 mg of MWCNTs@Fe_3O_4/PEI was mixed with Cr(VI) solution at constant pH value of 3 (with initial concentration of 50 mg L^{-1}). The above mixture in the conical flask was subject to shaking in a thermostatic shaker with a shaking rate of 150 rpm at 25^{o}C and the residual concentration of MO or Cr(VI) in the supernatant was determined at different time interval during the adsorption process to evaluate the kinetic process.

1.1.3. Adsorption isotherms and thermodynamics

For adsorption isotherms and thermodynamics, the batch experiments were carried out at three different temperatures (25, 40, and 55 ^{o}C) by varying the initial concentration of MO from 60 to 330

mg L^{-1} at pH value of 3 and that of Cr(VI) from 10 to 90 mg L^{-1} at pH value of 3. After shaking in a thermostatic shaker for 360 min and 240min, the adsorption equilibrium was achieved and the obtained equilibrium data were fitted using Langmuir and Freundlich isotherm models. The thermodynamic parameters including the Gibbs free energy, enthalpy and entropy were calculated on the basis of experimental data to evaluate the thermodynamic behavior of MO and Cr(VI) adsorption on as-prepared MWCNTs@Fe_3O_4/PEI adsorbent.

1.2. Adsorption experiments in binary system

The effect of co-existing Cr(VI) with initial concentration of 10 and 20 mg L^{-1} on adsorption isotherms of MO performed over the initial concentrations of MO ranging from 30 to 240 mg L^{-1} at pH 3 was evaluated. Conversely, in the presence of MO with concentrations of 20 and 40 mg L^{-1}, the adsorption isotherms of Cr(VI) within initial concentration range of 10-60 mg L^{-1} were also carried out in MO-Cr(VI) binary system at pH of 3 at 298 K. And other experimental conditions were similar to those of mono-component system described in **Section 1.1. (ESI).** Subsequently, the mutual effects between MO and Cr(VI) in binary system was determined by comparing the resulting adsorption isotherms for each pollutant with that obtained in mono-pollutant system at the same conditions.

2. Results and discussion

2.1. Effect of loading amount of PEI on adsorption

The PEI concentration used in the preparation of adsorbent may determine the loading amount of PEI in hybrid adsorbent, affecting the uptake performance of resulting material. Thus, the PEI amount varied from 0.5 to 7.0 g for the preparation of MWCNTs@Fe_3O_4/PEI was investigated in present work. The results shown in **Fig. S2** demonstrated that the removal ability of resulting

adsorbent for MO dramatically increased with increasing of PEI adding amount in the range of 0.5~2.4 g, and then maintained stable when PEI amount was above 2.4 g. It can be easily concluded that PEI loading amount plays a crucial role in promoting MO uptake by MWCNTs@Fe_3O_4/PEI. So, the appropriate PEI amount utilized for the preparation of target adsorbent was determined to be 2.4 g.

2.2. Effect of adsorbent dosage on adsorption

In order to get insight into the interactions between adsorbate and active sites of adsorbent in the solution, it is of great importance to determine the optimum adsorbent dosage[1]. The influence of adsorbent dosage on both removal rate and adsorption capacity of MWCNTs@Fe_3O_4/PEI toward MO and Cr (VI) is shown in **Fig. S3**. It is observed that the removal rate of MO increased greatly from 79 % to 98 % as the dosages of adsorbent increase from 3 to 9 mg, and then slowly reached a plateau with further increasing of adsorbent amount, which is presented in **Fig. S3a**. However, the adsorption capacity of MO decreases sharply from 1400 to 400 mg g^{-1} over the dosage ranging from 3 to 15 mg. Similar variation tendencies on removal rate and adsorption capacity were observed for Cr(VI) uptake by MWCNTs@Fe_3O_4/PEI in the adsorbent dosage range of 5-30 mg. The opposite effects of adsorbent dosage on removal rate and adsorption capacity can be explained as follows. Generally, the number of available adsorption sites multiplies with increasing of adsorbent dosage, thus causing the raise of removal efficiency. On the other hand, the number of unoccupied active adsorption sites increases as increasing of adsorbent dosage, resulting in the decrease of adsorption capacities of the adsorbent. Additionally, high amount of adsorbent may result in aggregation of adsorbent[2], further deteriorating the adsorption capacities of adsorbent. Thus, taking into account the satisfactory adsorption capacity as well as acceptable removal rate, the adsorbent dosage of 3 mg for

MO and 10 mg for Cr(VI) were selected for the subsequent experiments.

References

1 Y.-M. Hao, C. Man and Z.-B. Hu, *J. Hazard. Mater.*, 2010, **184**, 392–399.

2 Y.-T. Zhou, H.-L. Nie, C. Branford-White, Z.-Y. He and L.-M. Zhu, *J. Colloid Interface Sci.*, 2009, **330**, 29–37.

Figure captions

Fig. S1 EDS spectra and surface elemental composition of MWCNTs@Fe_3O_4/PEI

Fig. S2 Effect of loading amount of PEI on removal performance of MO (Conditions: initial dye concentration, 200 mg L^{-1} and 500 mg L^{-1}; adsorbent dosage, 10 mg; solution pH, 3; contact time, 6 h; temperature, 25 ℃; and agitation speed, 150 rpm).

Fig. S3 Effect of adsorbent dosage on removal efficiency of MO (a) and Cr(VI) (b) (Conditions: initial dye concentration, 200 mg L^{-1} for MO, 50 mg L^{-1} for Cr(VI); adsorbent dosage, 3~15 mg for MO, 5~30 mg for Cr(VI); solution pH, 3; contact time, 6 h; temperature, 25 ℃; and agitation speed, 150 rpm).

Fig. S4 Zeta potentials of MWCNTs, MWCNTs@Fe_3O_4, and MWCNTs@Fe_3O_4/PEI as a function of solution pH values.

Fig. S5 EDS spectra of MWCNTs@Fe_3O_4/PEI before and after adsorption of MO and Cr(VI).

Fig. S6 XPS spectra of MWCNTs@Fe_3O_4/PEI before and after adsorption of MO and Cr(VI).

Fig. S7 Evaluating the removal efficiency and reusability of MWCNTs@Fe_3O_4/PEI in model textile effluent. (Conditions: initial dye concentration, 200 mg L^{-1} for MO, 50 mg L^{-1} for Cr(VI); adsorbent dosage, 15 mg; solution pH, 3; contact time, 6 h ; temperature, 25 ℃; and agitation speed, 150 rpm).

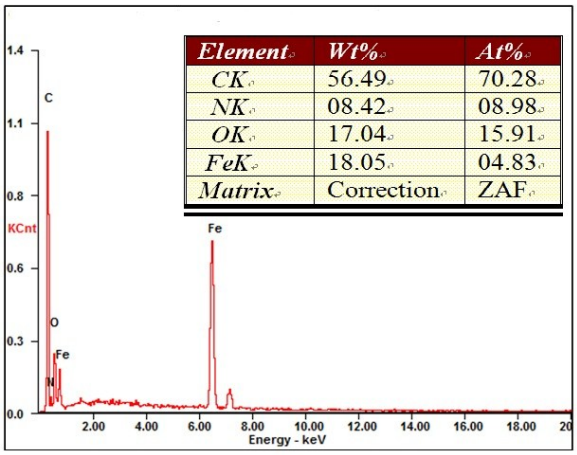
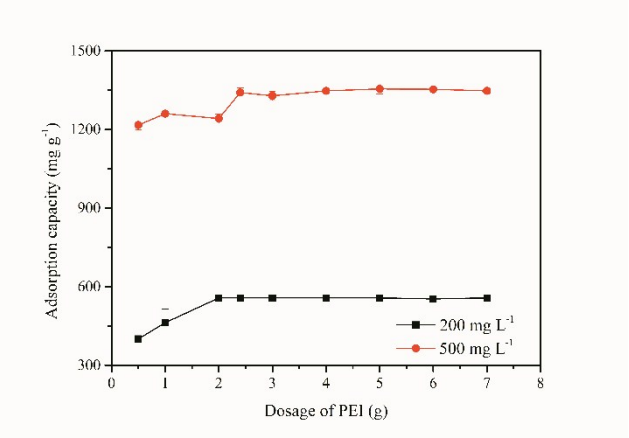


Fig. S1



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108 **Fig. S2**

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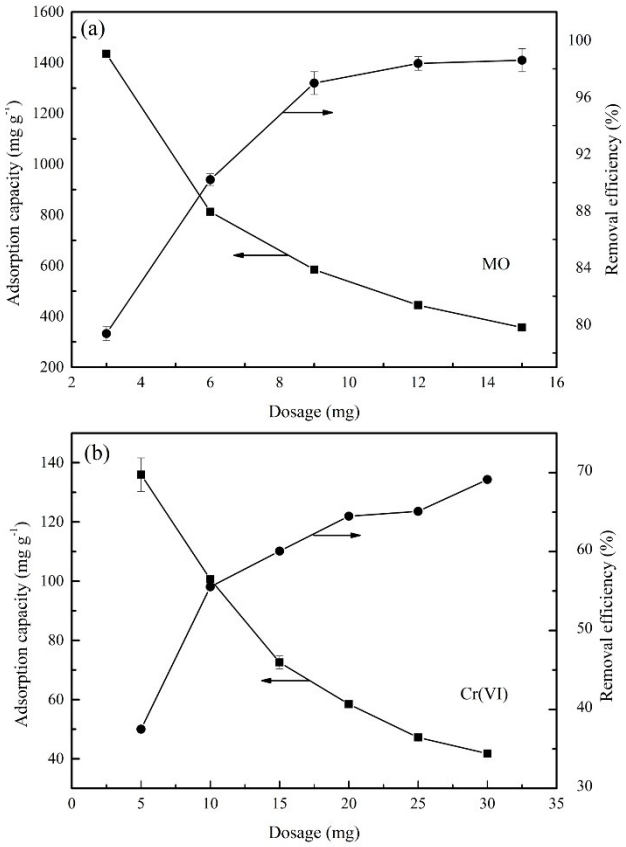
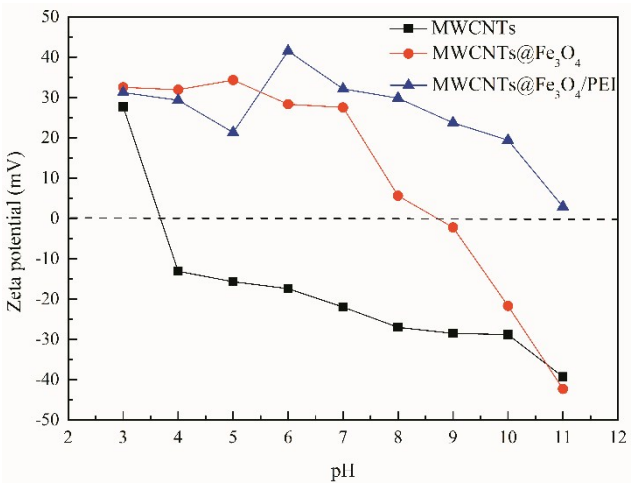


Fig. S3



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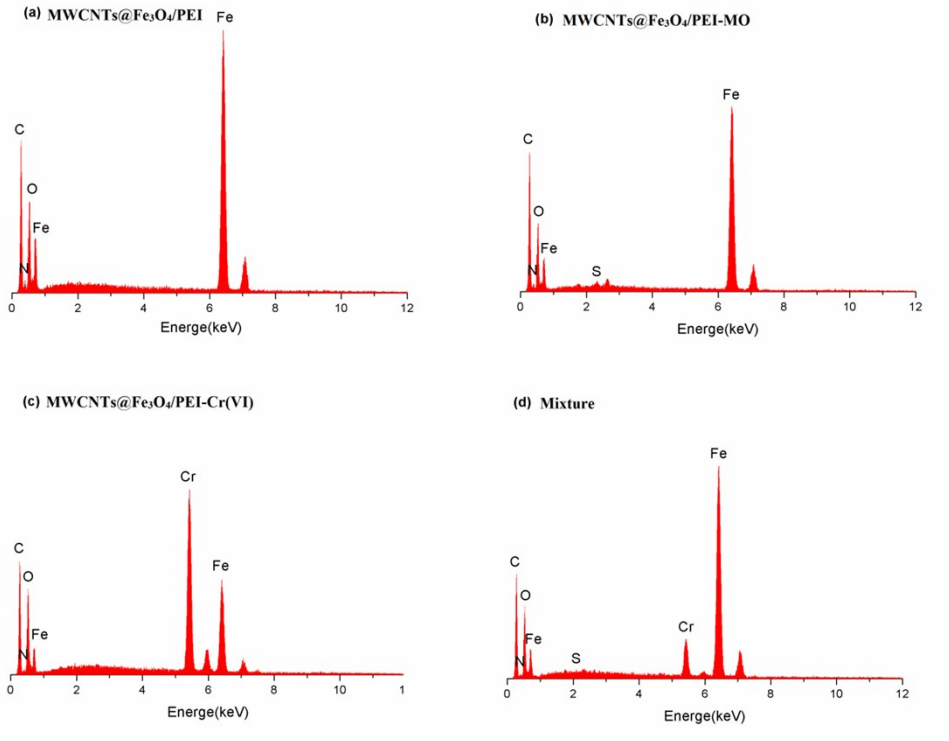
114 **Fig. S4**



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117 **Fig. S5**

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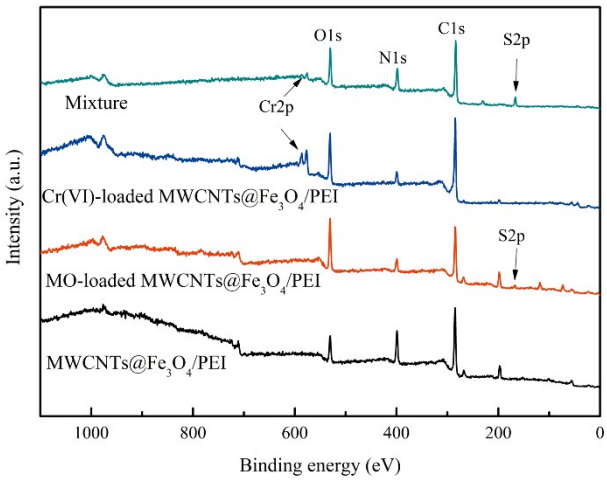

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120 **Fig. S6**

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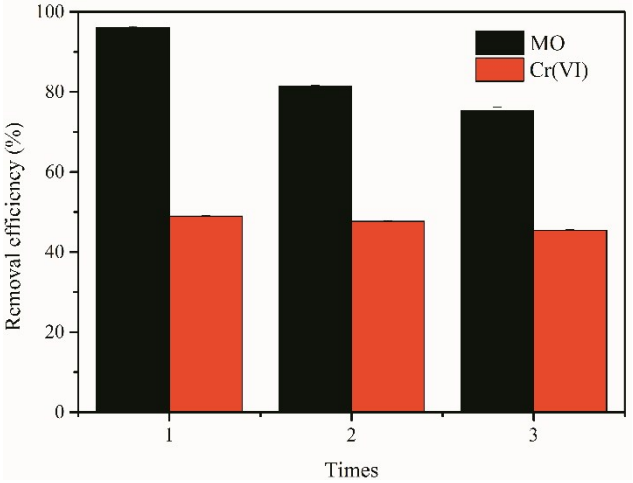

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123 **Fig. S7**

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