

Electronic Supplementary Information

The coked Ni/Al₂O₃ from the catalytic reforming of volatiles from co-pyrolysis of lignin and polyethylene: preparation, identification and application as a potential absorbent

Jing Zhao, †^a Zhanghong Wang, †^b Dekui Shen, *^a Chunfei Wu, *^c Kaihong Luo ^d and
Sai Gu ^e

^a Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, Jiangsu, PR China

^b College of Eco-Environmental Engineering, Guizhou Minzu University, Guiyang 550025, PR China

^c School of Chemistry and Chemical Engineering, Queen's University Belfast, Belfast, BT7 1NN, United Kingdom

^d Department of Mechanical Engineering, University College London, London, WC1E 7JE, United Kingdom

^e Faculty of Engineering and Physical Sciences, University of Surrey, Guilford, GU2 7XH, United Kingdom

Corresponding author e-mail: 101011398@seu.edu.cn (D. Shen), c.wu@qub.ac.uk (C. Wu).

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SECTION S1 The characterization of the raw materials

Table S1 Proximate analysis and ultimate analysis of raw materials concerning lignin and polyethylene.

	Ultimate analysis (%)				Proximate analysis (wt. %)		
	C	H	O	S	Fixed carbon	Ash	Volatile
lignin	61.65	5.59	31.3 ^a	1.46	28.14	1.88	66.52
polyethylene	84.64	15.36	- ^b	-	0.32	0.18	98.12

a is calculated by difference;

b represents below detection limit.

SECTION S2 The supplementary characterization results of the as-synthesized C-Ni/Al₂O₃-600°C composite

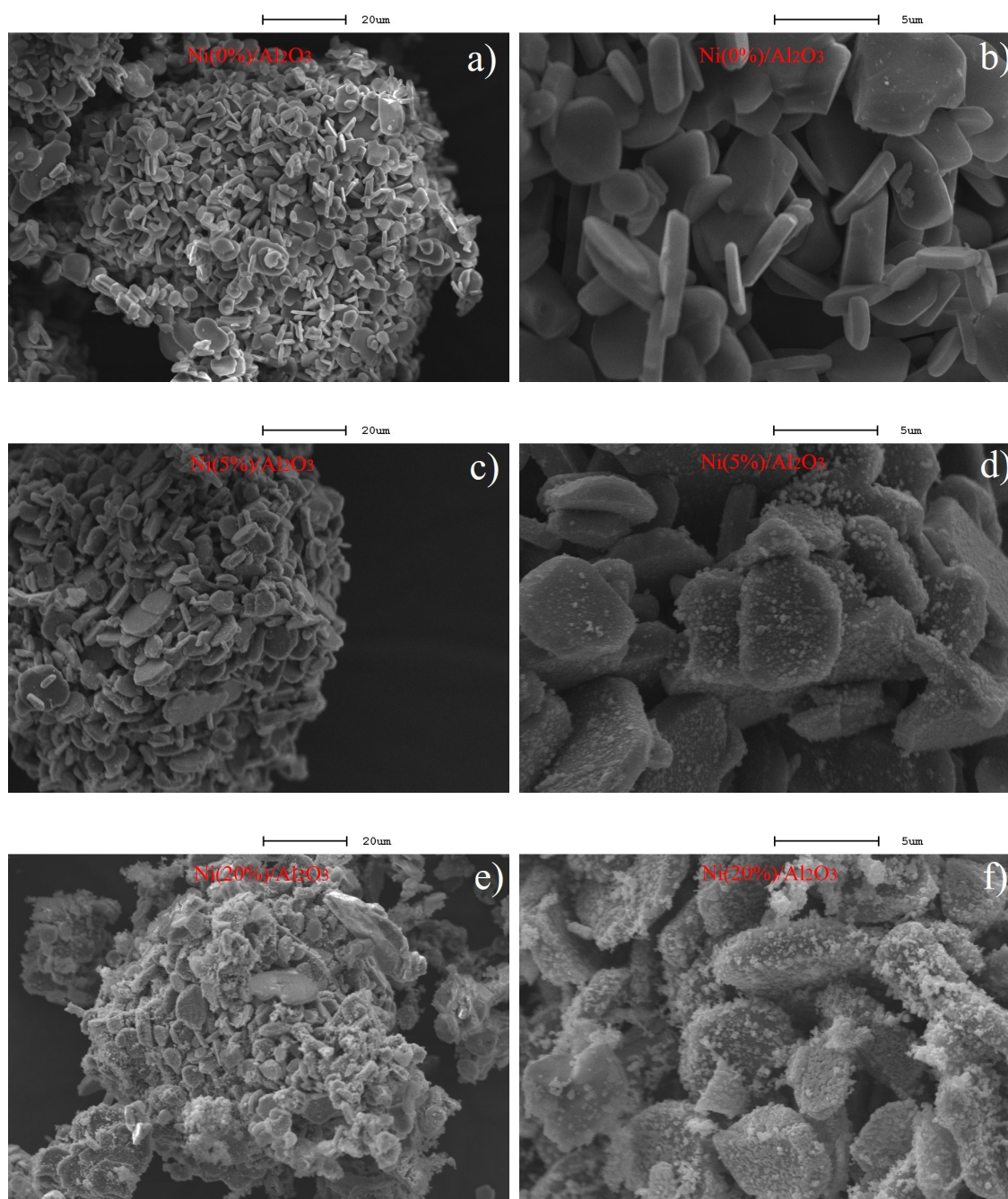


Fig. S1 SEM images of C-Ni/Al₂O₃-600°C composite with different Ni loadings on Al₂O₃, a-b) Ni(0%)/Al₂O₃; c-d) Ni(5%)/Al₂O₃ and e-f) Ni(20%)/Al₂O₃.

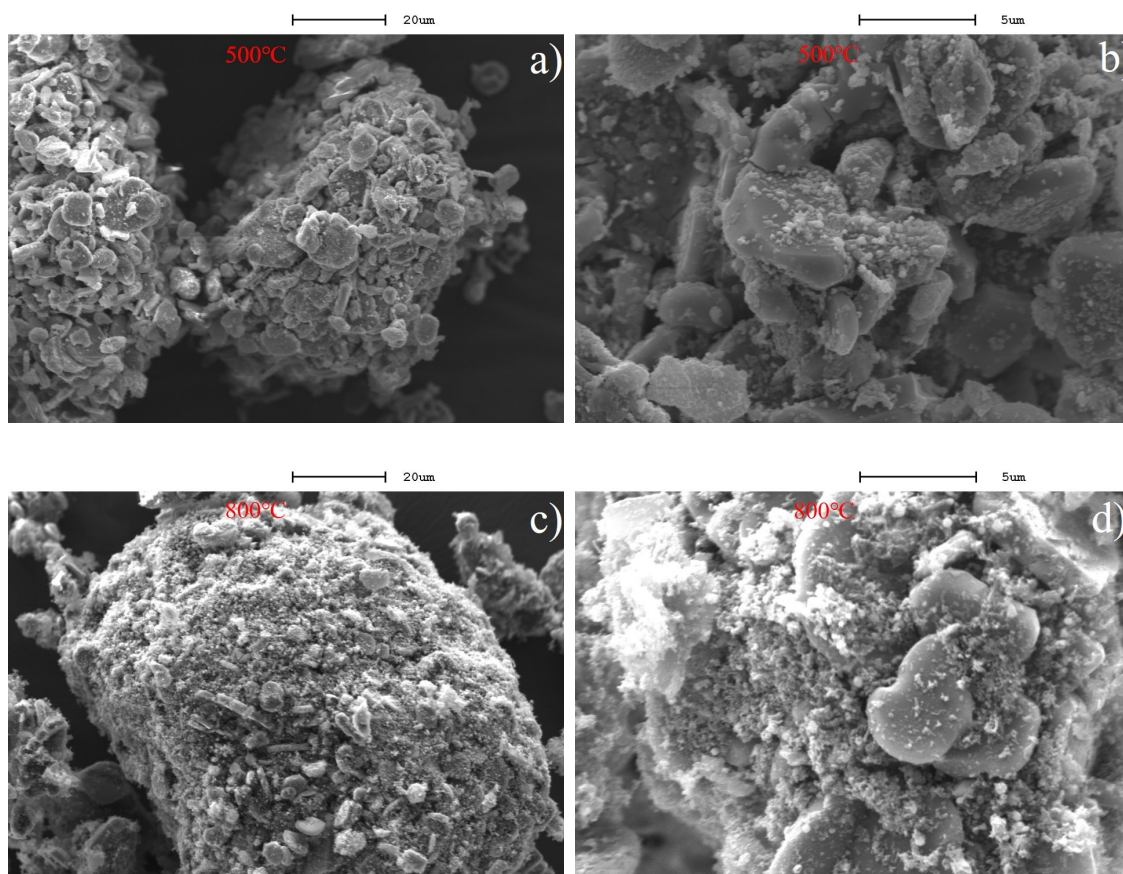


Fig. S2 SEM images of C-Ni(10%)/Al₂O₃ composite derived from catalytic reforming temperatures at 500 and 800 °C, a-b) 500 °C, c-d) 800 °C.

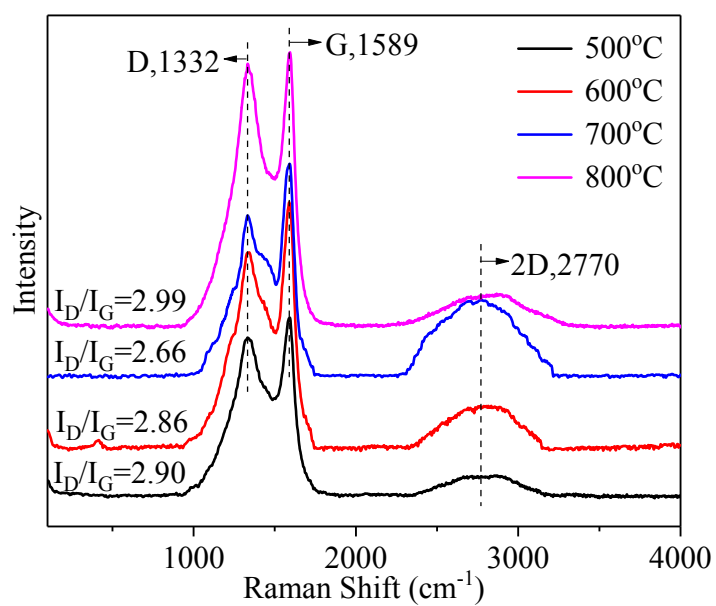


Fig. S3 Raman spectra of C-Ni(10%)/Al₂O₃ composite derived from different catalytic reforming temperatures.

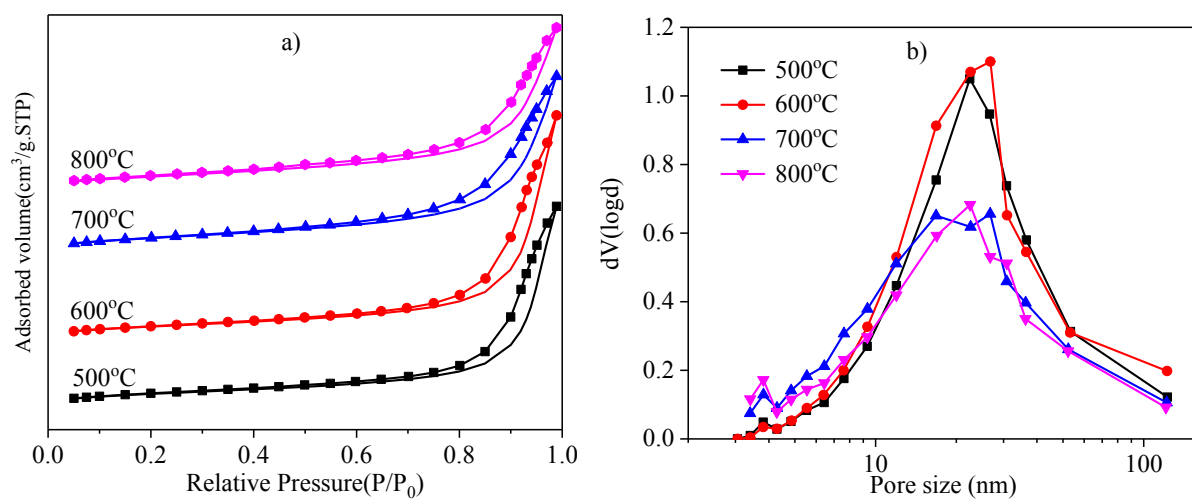


Fig. S4 N₂ adsorption/desorption isotherms and pore distribution of C-Ni(10%)/Al₂O₃ composite derived from different catalytic reforming temperatures.

SECTION S3 The effect of adsorption conditions on the adsorption performance of heavy metal ions and dyes

Effect of initial concentration

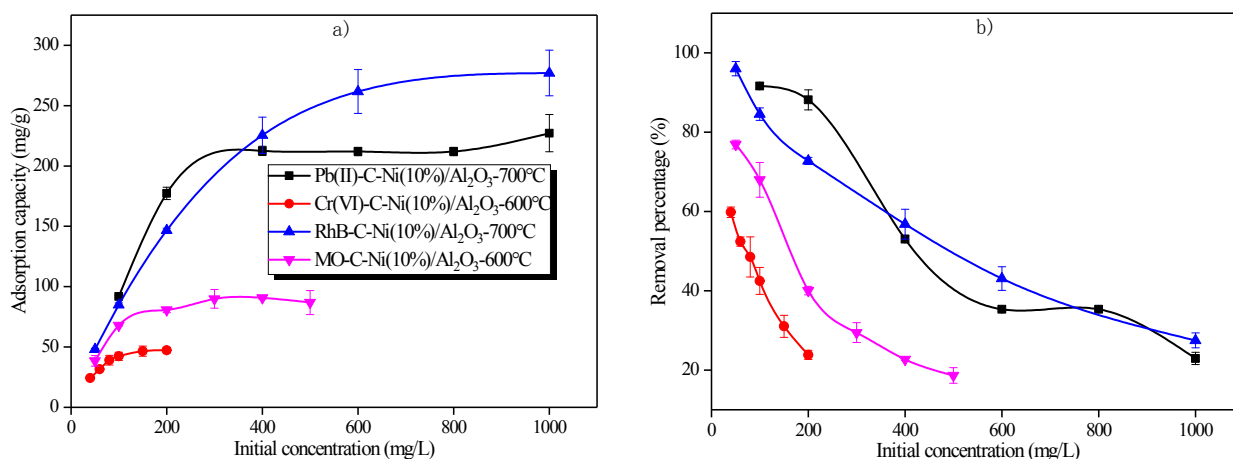


Fig. S5 The effect of initial concentration on the adsorption of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO).

The adsorption capacity and the removal percentage of the C-Ni/Al₂O₃ composite were highly influenced by the initial concentration of heavy metal ions and dyes in solution, which is exhibited in Fig. S5. As shown in Fig. S5a), the uptakes of the four pollutants using the C-Ni/Al₂O₃ composite as adsorbent were enhanced with the increase of initial concentration. The adsorption capacity of the C-Ni/Al₂O₃ composite for Pb(II) and Cr(VI) increased rapidly when the initial concentrations of Pb(II) and Cr(VI) were below 400 mg/L and 100 mg/L, respectively, while the increasing trend dramatically slowed down with the further increase of initial concentration. Similarly, the adsorbed amounts of RhB and MO increased significantly as the initial concentrations were below 600 mg/L and 300 mg/L, separately, and then slightly changed with the continuous increase of initial concentration. This phenomenon can be ascribed to that the increase of initial concentration in the initial stage provided higher driving force to overcome the mass transfer resistance of pollutants in solution,¹ and the surface active sites of the C-Ni/Al₂O₃ composite were completely consumed in the higher range of initial concentration.² In addition, it can be seen from Fig. S5b) that the removal percentage of Pb(II), Cr(VI), RhB and MO was remarkably decreased with the increasing initial pollutants concentration, which was clearly different from the change trend of adsorption capacity. This can be attributed to that both the driving force of the pollutants to promote adsorption and the residual

concentration of the pollutants in the aqueous solution were enhanced as the initial concentration of Pb(II), Cr(VI), RhB and MO increased.³ It should be mentioned that the set of the optimum initial concentration of heavy metal ions and dyes for adsorption in practical applications should give sufficient consideration to the adsorption capacity and removal percentage.

Effect of contact time

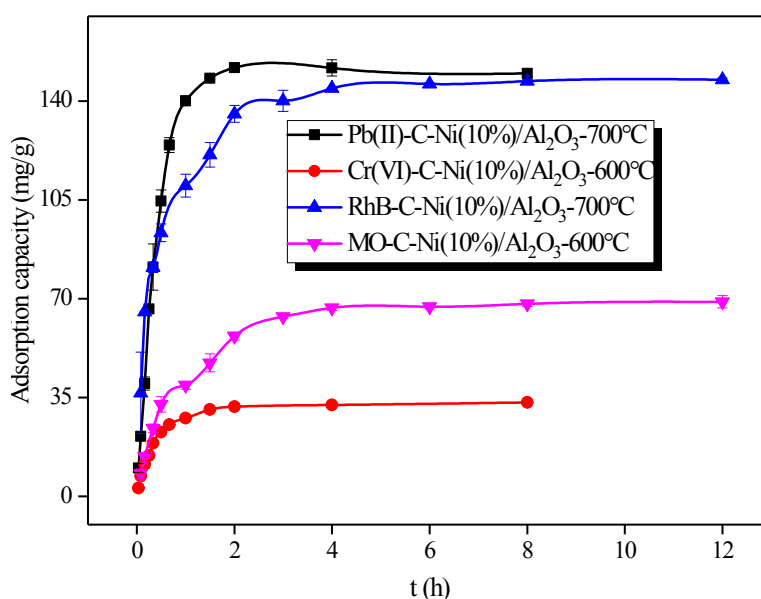


Fig. S6 The effect of contact time on the adsorption of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO).

The contact time has dramatic influence on the adsorption process of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO) by using C-Ni/Al₂O₃ composite (see in Fig. S6). The uptakes of Pb(II) and Cr(VI) at incipient 1 h accounted for about 92% and 83% of the equilibrium adsorption capacity, separately. Then, the adsorption gradually slowed down with the increase of contact time and reached a rough equilibrium in 2 h. Similarly, the same changing trend was also observed for the adsorption of RhB and MO, which was rapidly increased in the period of initial 1 h and leveled off in about 4 h. The high adsorption rate in initial contact time can be ascribed to the high availability of vacant adsorption sites, while with the continuous increasing of contact time, the vacancy active sites were saturated and the adsorption rate of heavy metal ions and dyes began to be limited by mass transport.^{4, 5}

Effect of ambient temperature

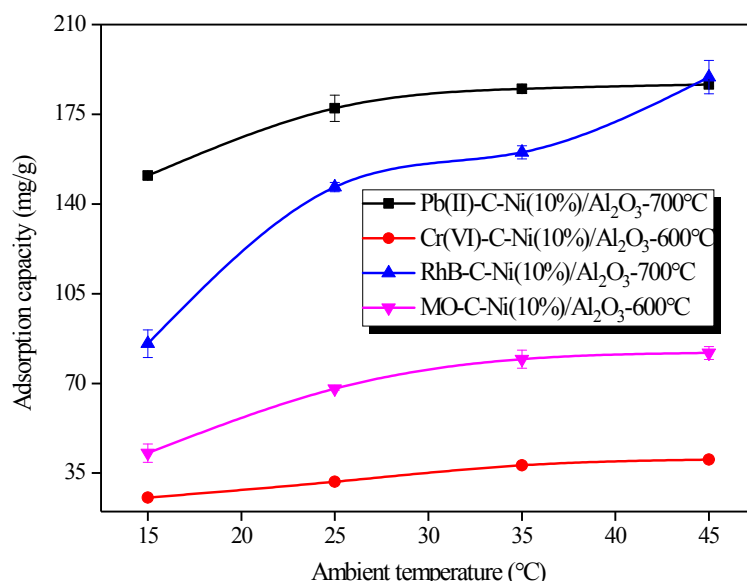


Fig. S7 The effect of ambient temperature on the adsorption of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO).

The adsorption performance of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO) onto C-Ni/Al₂O₃ composite at ambient temperature range from 15 °C to 45 °C was shown in Fig. S7. In general, the increase of ambient temperature accelerated the adsorption of Pb(II), Cr(VI), RhB and MO onto C-Ni/Al₂O₃ composite. As the temperature elevated from 15 °C to 45 °C, the uptakes of Pb(II) and Cr(VI) were increased from 151.08 and 25.46 mg/g to 186.68 and 40.28 mg/g, respectively, while the adsorption of RhB and MO was increased by 104.03 and 39.07 mg/g, separately. The enhancement of adsorption capacity with the increase of ambient temperature indicated that the adsorption process of heavy metal ions and dyes was endothermic. It is well known that ambient temperature has a significant effect on the random movement of adsorbate and the interactions between adsorbate and adsorbent.³ In consequence, the adsorption of heavy metal ions and dyes was enhanced at high ambient temperature because enough energy was provided to accelerate the movement of adsorbate and the interactions with the active sites of adsorbent.

Effect of pH

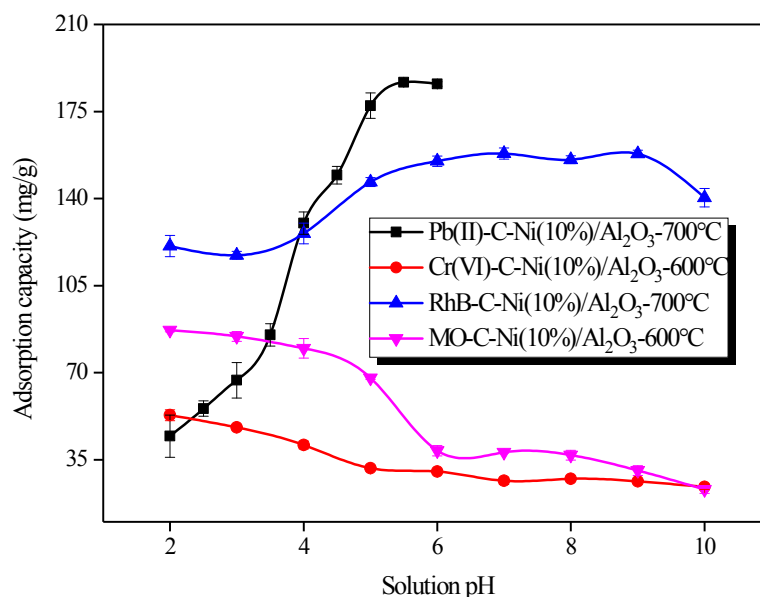


Fig. S8 The effect of pH on the adsorption of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO).

Solution pH, an important controlling factor in adsorption process, can influence the form of heavy metal ions and dye molecules in solution as well as the adsorbent surface charge and degree of ionization.⁶ It can be found from Fig. S8 that the influences of solution pH on the adsorption capacity of Pb(II), Cr(VI), RhB and MO onto C-Ni/Al₂O₃ composite were different. The adsorption capacity of Pb(II) was enhanced from 44.45 mg/g at the pH of 2.0 to 186.78 mg/g at the pH of 5.5 because of the increase of negatively charged groups on the adsorbent surface with the increase of pH.⁷ However, the uptake amount of Cr(VI) was decreased when the initial pH value of solution increased from 2 to 10. This can be ascribed to that the protonation of the active adsorption binding sites promoted the adsorption of Cr(VI) due to the electrostatic attraction at lower pH value, while when the pH value was elevated, an increase of OH⁻ concentration decreased the protonation level of the sorbent surface which accordingly decreased the Cr(VI) adsorption.⁸

The adsorption of RhB onto C-Ni/Al₂O₃ composite was in increasing trend with pH value elevated from 2 to 6, and maintained an approximate plateau over a pH range from 6 to 9. But increasing the solution pH value above 9 continuously decreased the adsorption of RhB from solution. The lower adsorption capacity of RhB at lower solution pH was attributed to the electrostatic repulsion between adsorbent

and RhB. This is because that RhB exists in a cationic form at low pH solution, while the adsorbent surface is positively charged due to the protonation of the surface functional groups.⁹ As depicted in Fig. S8, the adsorption capacity of MO decreased from 87.13 mg/g to 23.02 mg/g with the pH value increasing from 2 to 10. The decrease rate of MO adsorption was rapidly when the solution pH was below 6, and then became slowly as the solution pH increased from 6 to 10. In general, MO exists in anionic form at higher pH solution at the range from 6 to 10.⁹ The number of negatively charged sites on adsorbent surface was increased with the increase of the pH value, which had negative influence on the adsorption capacity of MO due to the electrostatic interaction. In addition, the competition between anionic dye and excess OH⁻ ions in the solution may also decrease the adsorption of MO at high pH value.¹⁰

SECTION S4 Equations used in present study

$$q_e = \frac{Q_m K_l C_e}{1 + K_l C_e} \quad \text{Eq. S1}$$

$$q_e = K_f C_e^{\frac{1}{n}} \quad \text{Eq. S2}$$

where q_e is the equilibrium adsorption capacity of heavy metal ions and dyes (mg/g), Q_m is the maximum capacity (mg/g), K_l is the Langmuir adsorption constant (L/mg), K_f is the Freundlich constant ($\text{mg}^{(1-n)} \text{L}^n \text{g}^{-1}$), and $1/n$ represents the Freundlich coefficient. C_e is the equilibrium concentration of heavy metal ions and dyes (mg/L).

$$\frac{dq_t}{dt} = k_1 (q_e - q_t) \quad \text{Eq. S3}$$

$$\frac{dq_t}{dt} = k_2 (q_e - q_t)^2 \quad \text{Eq. S4}$$

where t is the contact time (h), q_e and q_t refers to the adsorption capacity at equilibrium and at time t , respectively, (mg/g), k_1 and k_2 are the pseudo first order rate constant (h^{-1}) and the pseudo first order rate constant ($\text{g}/(\text{mg h})$), separately.

$$q_t = a \times t^{0.5} + b \quad \text{Eq. S5}$$

where t is contact time (h), q_t is the amounts of heavy metal ions and dyes adsorbed onto C-Ni/Al₂O₃ composite at time t (mg/g), a is the intra-particle diffusion rate constant (slope), b is the intercept.

$$\Delta G^0 = -RT \ln K_e \quad \text{Eq. S6}$$

$$K_e = \frac{q_e}{C_e} \quad \text{Eq. S7}$$

$$\ln K_e = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \text{Eq. S8}$$

where R is gas constant (8.314 J/(mol K)), T is temperature (K), K_e is Langmuir equilibrium constant, q_e is the concentration of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO) on carbon material composites at equilibrium (mg/g), C_e is the remaining concentration of heavy metal ions (Pb(II) & Cr(VI)) and dyes (RhB & MO) in solution at equilibrium (mg/L). Considering the relationship between ΔG^0 and K_e , ΔH^0 (kJ/mol) and ΔS^0 (J/(mol K)) can be calculated from the slope and intercept of

the plot of ΔG^θ versus T.

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