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Multifunctional Binding Sites on Nitrogen-Doped Carboxylated Porous Carbon for Highly Efficient Adsorption of Pb(II), Hg(II), and Cr(VI) Ions

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ABSTRACT: Heavy metal ions represent one of the most toxic and environmentally harmful pollutants of water sources. This work reports the development of a novel chelating nitrogen-doped carboxylated porous carbon (ND-CPC) adsorbent for the effective removal of the heavy metal ions Pb(II), Hg(II), and Cr(VI) from contaminated and polluted water sources. The ND-CPC adsorbent is designed to combine four different types of nitrogen functional groups (graphitic, pyrrolic, pyridinic, and pyridine oxide) with the carboxylic acid functional groups within a high surface area of $1135 \pm 20 \text{ m}^2/\text{g}$ of the porous carbon structure. The ND-CPC adsorbent shows exceptionally high adsorption affinity for Pb(II) with a capacity of 721 ± 14 mg/g in addition to high uptake values of 257 ± 5 and $104 \pm 2 \text{ mg/g}$ for Hg(II) and Cr(VI), respectively. The high adsorption capacity is also coupled with fast kinetics where the equilibrium time required for the 100% removal of Pb(II) from 50 ppb and 10 ppm concentrations is 30 s and 60 min, respectively. Even with the very high concentration of 700 ppm, 74% uptake of Pb(II) is achieved within 90 min. Removal efficiencies of 100% of Pb(II), 96% of Hg(II), 91% of Cu(II), 82% of Zn(II), 25% of



Cd(II), and 13% of Ni(II) are achieved from a solution containing 10 ppm concentrations of these ions, thus demonstrating excellent selectivity for Pb(II), Hg(II), and Cu(II) ions. Regeneration of the ND-CPC adsorbent shows excellent desorption efficiencies of 99 and 95% for Pb(II) and Cr(VI) ions, respectively. Because of the fast adsorption kinetics, high removal capacity and excellent regeneration, stability, and reusability, the ND-CPC is proposed as a highly efficient remediation adsorbent for the solid-phase removal of Pb(II), Hg(II), and Cr(VI) from contaminated water.

1. INTRODUCTION

The rapid increase in the world's population results in increasing waste and pollution, which also leads to serious water contamination. Consequently, the major sources of water contamination include chemicals, radioactive materials, pathogenic microbial substances, and heavy metals.¹⁻³ Recently, there has been an increasing global public health concern for environmental pollution caused by heavy metals.¹⁻⁴ The presence of toxic metal ions such as Pb(II), Hg(II), and Cr(VI) in water sources is a threat to the environment and to human life because of their refractory degradation, ease of entering the food chain, and high toxicity that can cause several chronic and severe diseases including cancer and hypertension.¹⁻⁴ Lead contamination is considered to be among the most serious water contamination problems because according to the most recent analysis by UNICEF, 30% of the world's 2.4 billion children and adolescents have a higher blood lead level than the normal health level in the United States.⁵ The maximum permissible lead level in domestic water according to the U.S. Environmental Protection Agency is 15 ppb.³ Clearly, there is an immediate need to develop highly efficient methods to extract toxic metal ions including Pb(II) from polluted and treated water.

A variety of techniques are currently available for the extraction of heavy metal ions from aqueous solutions including ion exchange, solvent extraction, membrane separation, electrodeposition, chemical precipitation, coagulation, flotation, irradiation, ozonation, and adsorption.³ Adsorption by chelating resins is one of the best-used and promising methods because of its low cost, ease of application, and scalability compared to other methods which can be inefficient and costly or require complicated processing and modifications. Furthermore, adsorption methods tend to generate high-quality treated effluent and offer flexibility in operation and design. Additionally, used adsorbents can occasionally be regenerated by an appropriate desorption process which allows for using the adsorbent several times because of the reversible characteristics of adsorption. However, traditional absorbents such as activated carbon, clay,

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and activated alumina or silica exhibit limited adsorption abilities and poor selectivity for highly toxic metal ions, especially Pb(II), Hg(II), and Cr(VI).^{7–9} Thus, it is crucial to develop new adsorbents with specific active sites as well as high surface areas to ensure high selectivity and high adsorption capacity of Pb(II), Hg(II), and Cr(VI) from contaminated water.

Nitrogen-doped carbon (NDC) materials have attracted increased attention as catalysts and adsorbents of heavy metals because of their unique chelating structures, high surface area and pore volume, large adsorption capacity, fast adsorption kinetics, mechanical and thermal stability, and cost-effective preparation methods.^{10–17} Recently, several new NDC materials have been developed for water treatment such as nitrogen-doped magnetic carbon nanoparticles,¹⁰ NDC nanofibers,¹¹ NDC xerogels,¹² nitrogen-doped magnetic carbon,¹³ nickel ferrite bearing nitrogen-doped mesoporous carbon,¹⁴ NDC dots,¹⁵ NDC nanotubes,¹⁶ and NDC-encapsulated molybdenum carbide.¹⁷

In the present work, we introduce a novel NDC adsorbent, namely, nitrogen-doped carboxylated porous carbon (ND-CPC) for the efficient removal of heavy metal ions from aqueous solutions with a remarkably high adsorption capacity for Pb(II). The approach presented here for the incorporation of the pyridinic, pyrrolic, graphitic, and pyridine oxide nitrogen-based chelating agents within the activated porous carbon framework has never been reported before. Therefore, the goal of the present work is to develop the ND-CPC adsorbent as an effective chelating agent for Pb(II) and other toxic metal ions such as Hg(II) and Cr(VI) and to demonstrate its facile regeneration for the large-scale application in the removal of toxic metal ions from contaminated water sources.

2. EXPERIMENTAL SECTION

2.1. Materials. All reagents were of analytical grade and used without further purification as received from Sigma-Aldrich: melamine (99.999%), formaldehyde (99%), sodium hydroxide (99%), acetic acid (99%), nitric acid (99%), hydrochloric acid (99%), and ethanol (99%). Stock solutions of several concentrations of Pb(NO₃)₂, CuCl₂·2H₂O, HgCl₂, CdCl₂, KH₂AsO₄, K₂Cr₂O₇, Ni(NO₃)₂·6H₂O, and Zn(NO₃)₂. 6H₂O were used as sources for the Pb(II), Cu(II), Hg(II), Cd(II), As(V), Cr(VI), Ni(II), and Zn(II) ions, respectively.

2.2. Synthesis of ND-CPC. Melamine-formaldehyde resin (MF-R) was prepared by dispersing 4.2 g of melamine in 40 mL of deionized (DI) water and adding 7.5 g of formaldehyde to the solution at pH 10.5. The solution was heated under reflux to 80 °C and stirred until a colorless solution was obtained. The reaction was then quenched by the addition of 2 mL of acetic acid and stirred under reflux at 90 °C for 5 h. Finally, the solution was cooled to room temperature, centrifuged, washed consecutively with both DI water and ethanol, and dried at 60 °C overnight.¹⁸ Two grams of MF-R was placed in a calcination crucible boat and was transferred to a temperature-programmed tube furnace where carbonization was performed at 800 °C for 3 h with a heating rate of 5 °C/ min under a nitrogen atmosphere. The black carbon product nitrogen-doped porous carbon (ND-PC) was oxidized with 2 mL of concentrated nitric acid under reflux at 80 °C for 3 h. The final product, ND-CPC, was washed repeatedly with 0.01 M NaOH and then with DI water and dried overnight in the oven at 60 °C.

2.3. Characterization. The Fourier transform infrared (FT-IR) and Raman spectra were measured using the Nicolet-Nexus 670 FT-IR diamond attenuated total reflectance (DATR) and the Thermo Scientific DXR Smart Raman spectrometers with 532 nm excitation, respectively. Powder Xray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) were performed using the PANalytical MPD X'Pert PRO diffractometer and the Thermo Fisher Scientific ESCALAB 250 spectrometer, respectively. The nitrogen adsorption-desorption isotherms were obtained at 77 K using a Micromeritics 3Flex instrument. Transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images were obtained at 100 kV by using the JEOL JEM-1400 and Hitachi SU-70 field-emission scanning electron microscopes, respectively. The concentrations of heavy metals in solutions before and after removal experiments were quantified by using either the Varian Vista-MPX inductively coupled plasma optical emission spectroscope with a charged coupled detector for simultaneous detection at ppm concentration levels or with the Agilent 8900 triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS) with an electron multiple detector for detection at the ppb concentration levels.

2.4. Removal of Heavy Metal Ions. q_{e} , the adsorbed amount of metal per unit mass of the adsorbent, and % R_{e} , the percentage of metal removal, are calculated using eqs 1 and 2, respectively.¹⁹

$$q_{\rm e} = \frac{(C_0 - C_{\rm e})V}{m} \tag{1}$$

$$\% R_{\rm e} = \frac{(C_0 - C_{\rm e})}{C_0} \times 100$$
⁽²⁾

where C_0 is the initial concentration of metal ions in the solution (mg/L), C_e is the equilibrium concentration (mg/L) after adsorption, q_e is the adsorption capacity (mg/g), V is the volume of the solution (L), and m is the mass of the adsorbent (g).

2.5. Desorption Studies. Metal-loaded adsorbents were collected from the suspension by centrifuging, washing with DI water, and drying at 60 °C. 5 mg of the loaded adsorbent was placed in different glass vials containing 5 mL of different eluents (0.1, 0.5, and 1.0 M HNO₃ or NaOH), and the mixture was agitated for 5 h at 25 °C. ICP–OES was used to determine the final concentration of lead ions in the eluent, and the desorption efficiency was calculated using eq 3.¹⁹

$$\% D_{\rm e} = \frac{C_{\rm d} V}{q_{\rm e} m} \times 100 \tag{3}$$

where C_d is the concentration of metal ions after desorption, V is the volume of the eluent (L), q_e is the adsorption capacity (mg/g), and m is the mass (g) of the adsorbent.

3. RESULTS AND DISCUSSION

3.1. Adsorbent Design Approach. The design strategy for the preparation of the ND-CPC adsorbent is based on three main steps: (1) formation of the MF-R by a polymerization reaction between melamine and formalde-hyde,²⁰ (2) carbonization of MF-R at 800 °C under a nitrogen atmosphere to form ND-PC,²¹ and finally (3) chemical oxidation of ND-PC by nitric acid to form ND-CPC. This unique design strategy results in the formation of the ND-CPC

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Scheme 1. General Approach for the Synthesis of ND-CPC



Figure 1. (A) XRD patterns, (B) Raman spectra, and (C) FT-IR spectra of the MF-R, ND-PC, and ND-CPC adsorbents.

adsorbent containing four different types of nitrogen functional groups (graphitic, pyrrolic, pyridinic, and pyridine oxide) as well as carboxylic acid functional groups within the activated porous carbon structure. Both the nitrogen-containing and the carboxylic acid functional groups are strong chelating agents for heavy metal ions in contaminated water.^{10–12} Scheme 1 illustrates the general procedure for the synthesis of the ND-CPC adsorbent.

3.2. Characterization of the MF-R, ND-PC, and ND-CPC Adsorbents. Figure 1A displays the XRD patterns of the MF-R, ND-PC, and ND-CPC adsorbents showing two broad characteristic peaks corresponding to the (002) and (001) diffraction planes from the graphitic pore walls. These peaks appear at $2\theta = 22$ and 41° for the MF-R adsorbent and are observed to shift to higher 2θ values of 26.3 and 44° in the ND-PC and ND-CPC adsorbents, respectively, because of the formation of highly graphitic ordered carbon networks during the carbonization process of the MF-R.²² Moreover, the XRD patterns of ND-PC and ND-CPC are exactly the same, which

means that oxidation by nitric acid does not affect the order of the graphitic structure in these adsorbents.

The Raman spectrum of MF-R, displayed in Figure 1B, shows three characteristic peaks at 970, 1431, and 2950 cm⁻¹ corresponding to the triazine ring breathing, $(N-CH_2-O)$ breathing, and (-CH-) stretching vibrations, respectively.²³ The spectra of ND-PC and ND-CPC show two broad peaks at 1344 and 1585 cm⁻¹ associated with defects and disorder (D-band) and the stretching vibrations of the conjugated C==C groups in carbon materials (G-band), respectively. For the ND-PC and ND-CPC adsorbents, the intensity ratio (I_D/I_G) is 1.05 and 1.07, respectively, suggesting the presence of significant defects and vacancies in both the ND-PC and ND-CPC materials, which can enhance the adsorption capacity of heavy metal ions from aqueous solutions toward these adsorbents.^{14,21}

The FT-IR spectrum of MF-R, displayed in Figure 1C, shows an absorption peak at 3364 cm^{-1} assigned to the stretching vibration of (N–H) groups in the structure. In

addition, the peaks at 2946 and 977 cm⁻¹ are due to the (-CH) stretching vibration in the CH₂ groups and the (C-O) vibration, respectively. Moreover, the peaks at 1578, 1498, 1340, and 815 cm⁻¹ are due to the ring vibrations of the melamine triazine ring.^{18,24} Both the ND-PC and ND-CPC spectra show absorption bands at around 2636, 2320, 1571, 1260, and 1080 cm⁻¹ corresponding to the stretching vibrations of the C=N, C-N, C=C, N-O, and C-H groups, respectively, in the graphitic, pyridinic, pyrrolic, and pyridine oxide heterocycles. Also, the spectrum of the ND-CPC adsorbent shows two additional peaks at 3300 and 1770 cm⁻¹ corresponding to the stretching vibrations of (O-H) and (C=O) of the carboxylic acid groups formed after the chemical oxidation step of ND-PC.^{20,21,24}

The presence of the nitrogen functional groups pyridinic, pyrrolic, graphitic, and pyridine oxides in ND-PC and ND-CPC, and the carboxylic acid groups in ND-CPC are also evident by the XPS data shown in Figure 2 and S1 (Supporting



Figure 2. (A) XPS survey spectrum of ND-CPC and XPS high-resolution spectra of (B) C 1s, (C) N 1s, and (D) O 1s.

Information). The survey scans of ND-PC (Figure S1A) and ND-CPC (Figure 2A) show three typical peaks of C 1s (285 eV), N 1s (400 eV), and O 1s (531 eV). From these data, the atomic contents of C, N, and O are determined as 86.3, 9.4, and 4.3%, respectively, in the ND-PC, and 78.1, 8.4, and 13.6% in the ND-CPC adsorbents (Table S1). The increase in the oxygen content from 4.3% in ND-PC to 13.6% in ND-CPC is due to the carboxylic acid functional groups formed after the nitric acid oxidation treatment of ND-PC. The C 1s spectrum of ND-CPC (Figure 2B) can be deconvoluted into four peaks at 284.6, 285.9, 287.4, and 289.8 eV representing the C 1s photoelectrons in C=C, C=N/C-O, C-N/C=O, and -COOH groups, respectively.²⁵ The N 1s spectrum of ND-CPC (Figure 2C) displays four peaks at 398.1, 399.5, 400.2, and 405.1 eV, which can be ascribed to pyridinic, pyrrolic, graphitic, and pyridine oxides, respectively.^{26,27} Figure 2D shows the spectrum of O 1s of ND-CPC which can be deconvoluted into three peaks at 531.1, 532.6, and 535 eV assigned to O=C, O-C, and O-N, respectively.^{28,29} Figure S1B-D show the spectra of C 1s, N 1s, and O 1s in the ND-PC adsorbent. These spectra resemble the ND-CPC spectra

except that the peaks related to the carboxylic acid functional groups are not present in the ND-PC spectra. For example, the C 1s spectrum of ND-PC (Figure S1B) is deconvoluted into only three peaks at 284.6, 285.9, and 287.4 eV corresponding to C=C, C=N, and C-N groups, respectively, and there is no peak at 289.9 eV for the -COOH group. Similarly, the O 1s spectrum of ND-PC (Figure S1D) has only one peak at 535 eV because of the O-N group and there are no peaks for carboxylic acid groups at 531.1 eV (O=C) or 532.6 eV (O-C). Therefore, both the FT-IR and XPS spectra confirm the presence of carboxylic acid groups functionalized within the ND-CPC adsorbent after the chemical oxidation step of ND-PC PC by nitric acid.

The Brunauer-Emmett-Teller surface areas of the MF-R, ND-PC, and ND-CPC adsorbents, measured by N_2 adsorption-desorption isotherms (Figure S2A and Table S2, Supporting Information) show that the ND-CPC adsorbent has a much higher value $(1135 \pm 20 \text{ m}^2/\text{g})$ than the ND-PC $(462 \pm 8 \text{ m}^2/\text{g})$ or the MF-R $(82 \pm 2 \text{ m}^2/\text{g})$ adsorbents. The estimated pore volume distributions of the MF-R, ND-PC, and ND-CPC adsorbents are shown in Figure S2B–D, respectively. Interestingly, the adsorption-desorption isotherm profiles of the three adsorbents are very different, as shown in Figure S2A. The MF-R profile exhibits a hysteresis loop at a high relative pressure because of the mesoporous structure of the resin with a pore size greater than 2 nm consistent with the type IV isotherm.³⁰ The ND-PC adsorbent shows a combination of type I and type IV isotherms where the significant uptake at very low relative pressure is consistent with type I, while the hysteresis loop at intermediate and high relative pressure corresponding to the adsorption in mesopores is more consistent with the type IV isotherm.^{30,32} The ND-CPC isotherm clearly follows type I where the high adsorption capacity at very low relative pressure is followed by a plateau at a higher relative pressure due to the adsorption in micropores with a pore size less than 2 nm.³⁰ Therefore, the surface area and pore volume of ND-CPC (1135 m²/g and 0.551 cm³/g, respectively) are much higher than either the ND-PC (461 m^2/g and 0.098 cm³/g, respectively) or the MF-R (82 m²/g and 0.065 cm^3/g , respectively) adsorbent. The significant increase in surface area and pore volume from MF-R to ND-PC could be attributed to the carbonization of MF-R at 800 °C, which generates highly ordered micropores and mesopores in ND-PC, while the increase from ND-PC to ND-CPC might be due to the nitric acid treatment of ND-PC.^{30,32} The nitric acid treatment of ND-PC results in the release of gases most likely CO₂ and NO₂, which could contribute to the increased porosity of ND-CPC. The nitric acid treatment also results in cleaning the ND-PC surface from carbon and other impurities that can block the pores and also in generating new pores and introducing hydrophilic functional groups such as hydroxyl and carboxylic groups within the ND-CPC structure.^{25,30,31}

SEM and TEM images of the ND-CPC adsorbent, displayed in Figure 3, clearly indicate that the adsorbent has a highly porous surface resulting from the nitric acid treatment during the chemical oxidation step of ND-PC. In contrast, the MF-R adsorbent exhibits a nonporous structure as shown in the SEM and TEM images displayed in Figure S3 (Supporting Information). Also, the ND-PC adsorbent exhibits a much less porous structure compared to the ND-CPC adsorbent as shown in the SEM and TEM images displayed in Figure S4 (Supporting Information). The surface composition of the ND-CPC adsorbent determined by energy-dispersive X-ray



Figure 3. SEM (A,B) and TEM (C,D) images of the ND-CPC adsorbent.

spectroscopy (EDX) (Figure S5) indicates C, N, and O weight percentages of 48.3, 13.6, and 24.8%, respectively, which appear to be consistent with the atomic percentages of 78.1% (C), 8.4% (N), and 13.6% (O), determined from the XPS survey scan of ND-CPC.

3.3. Adsorption Capacity of ND-CPC for Heavy Metal lons. Figure 4A illustrates the effect of pH on the removal of the metal ions by the ND-CPC adsorbent. For Pb(II), Hg(II), Cu(II), and Cd(II), the maximum sorption capacity observed at pH 5.0–6.0 can be explained by the protonation of the binding sites of the adsorbent at low pH which creates a highly positive surface charge on the adsorbent and increases the repulsive forces between the adsorbent and the positive ions. As the pH increases, the negative surface charge on the adsorbent increases and the attractive forces with the positive ions become stronger, thus resulting in an increase in the removal efficiency. However, for As(V) and Cr(VI), the adsorption capacity increases at pH between 1.0 and 3.0, and the maximum adsorption occurs at pH 3. This can be explained by the strong electrostatic attractions between the anionic species $[H_2AsO_4]^-$ and $[HCrO_4]^-$ and the protonated oxygen and nitrogen functional groups on the surface of the ND-CPC adsorbent at low pH.^{13,19,32}

The effects of the initial concentrations of Pb(II), Hg(II), Cr(VI), Cd(II), Cu(II), and As(V) on the adsorption capacity of ND-CPC are shown in Figure 4B–D. A 100% removal efficiency of Pb(II) at pH 6 is observed not only at very low initial concentrations such as 25-1000 ppb (Figure 4B) but also at higher concentrations up to 300 ppm, as shown in Figure 4C. The maximum adsorption capacity of 721 ± 14 mg/g is reached when using very high concentrations of 1000-1700 ppm of Pb(II), as shown in Figure 4C. The removal efficiency for Hg(II) at pH 6 is 100% for initial concentrations of 10-100 ppm, and the maximum adsorption capacity of 257 mg/g is reached at a high concentration of 1000 ppm. The removal efficiencies for Cr(VI) at pH 3 are 80 and 84% for initial concentrations of 10 and 25 ppm,



Figure 4. (A) Effect of the solution pH on the adsorption capacity of ND-CPC for Pb(II), Hg(II), Cr(VI), Cu(II), Cd(II), and As(V) {conditions: $C_0 = 100 \text{ mg/L} [Pb(II)]$, 50 mg/L [Hg(II), Cr(VI), Cu(II), Cd(II), As(V)]; T = 298 K; adsorbent dose = 0.005 g/5 mL}. (B) Dependence of the removal efficiency of Pb(II) on the initial concentration [$C_0 = 25-1000 \mu g/L$]. (C,D) Effect of initial concentrations on the removal of Pb(II), Hg(II), Cr(VI), Cu(II), Cd(II), and As(V) ions on ND-CPC [conditions: $C_0 = 10-1700 \text{ mg/L} Pb(II)$, 10–1000 mg/L Hg(II), 10–500 mg/L Cr(VI), 10–300 mg/L Cu(II), Cd(II), and As(V); pH 6 for Pb(II), Hg(II), Cd(II), and Cu(II), pH 3 for Cr(VI) and As(V); T = 298 K; adsorbent dose = 0.005 g/5 mL].



Figure 5. % removal of metal ions by ND-CPC as a function of contact time for (A) Pb(II) at 50 ppb, (B) Pb(II) at 10 ppm, (C) Pb(II) at 700 ppm, and (D) Hg(II), Cr(VI), Cu(II), Cd(II) and, As(V) at 200 ppm [conditions: pH 6 for Pb(II), Hg(II), Cd(II), and Cu(II), pH 3 for Cr(VI) and As(V); adsorbent dose = 0.005 g/5 mL; T = 298 K].

respectively, and the maximum adsorption capacity of 104 mg/ g is reached at a concentration of 500 ppm. The removal efficiencies for Cd(II) and Cu(II) at pH 6 and for As(V) at pH 3 (all from initial concentrations of 10 ppm) are 90, 70, and 50%, respectively. The maximum adsorption capacities for Cd(II), Cu(II), and As(V) are 27 ± 0.5 , 20 ± 0.4 , and $14 \pm$ 0.3 mg/g, respectively, from the initial concentration of 300 ppm. These results demonstrate the high potential of the ND-CPC adsorbent for water treatment over a very wide range of metal ion concentrations. The high adsorption capacity of ND-CPC for Pb(II), Hg(II), and Cr(VI) ions can be attributed to the multiple nitrogen and oxygen functional groups on the ND-CPC surface, which act as strong coordination sites for forming stable complexes with these metal ions.

To prove the remarkable efficiency of ND-CPC for the Pb(II) removal compared to that of the MF-R and ND-PC adsorbents, the effect of concentration was studied for MF-R and ND-PC under similar conditions to those used for ND-CPC. As shown in Figure S6 and Table S3 (Supporting Information), the maximum adsorption capacities were 721 \pm 14, 389 \pm 8, and 242 \pm 5 mg/g for ND-CPC, ND-PC, and MF-R, respectively. The high adsorption capacity for ND-CPC could be attributed to the high surface area (1135 \pm 20 m²/g) as compared to ND-PC (462 \pm 8 m²/g) and MF-R (82 \pm 2 m²/g) as well as to the carboxylic acid functional groups which were generated after the chemical oxidation step by the nitric acid to chelate the lead ions directly from the solution.

The effect of contact time on the removal of Pb(II), Cu(II), Hg(II), Cd(II), As(V), and Cr(VI) ions by the ND-CPC adsorbent is shown in Figure 5. At a very low concentration of 50 ppb Pb(II), the removal efficiency is 100% after 30 s contact time as shown in Figure 5A which proves the tremendous ability for ND-CPC as an efficient adsorbent at low Pb(II) concentrations in polluted water. When the concentration of Pb(II) ions is increased from 10 to 700 ppm, the contact time required to reach 100 and 74% removal efficiency is increased from 60 to 90 min, respectively, as

shown in Figure 5B,C. However, for Hg(II), Cr(VI), Cd(II), Cu(II), and As(V), a contact time of about 200 min is required to reach equilibrium and to achieve removal efficiencies of 65, 31, 15, 9, and 7%, respectively, from initial concentrations of 200 ppm for each metal ion.

The adsorption data of the studied metal ions fit well with the Langmuir-isotherm model, as shown in Figure S7A (Supporting Information). The maximum adsorption capacities (q_{max}) for Pb(II), Hg(II), Cr(VI), Cd(II), Cu(II), and As(V) at 25 °C are calculated to be 783.0, 257.4, 104.0, 27.5, 20.2, and 14.7 mg/g, respectively, in excellent agreement with the experimental values as shown in Table S4 (Supporting Information). The excellent agreement with the Langmuir model suggests that the adsorption is homogeneous with a monolayer coverage of the adsorbent.¹⁹ The adsorption kinetics are well described by the pseudo-second-order kinetic model for the studied heavy metal ions as shown in Figure S7B and Table S5 (Supporting Information). The bimolecular interaction between the adsorbent and the adsorbate involves sharing and exchange of electrons provided by the strong chelating functional groups (basic nitrogen and oxygen atoms) within the ND-CPC adsorbent.

SEM images coupled with the EDX analysis of the ND-CPC adsorbent indicate that the porosity of the adsorbent is reduced after the adsorption of the Pb(II) ions as shown in Figure S8A,B (Supporting Information).

3.4. Mechanism for Pb(II) and Cr(VI) Uptake by the ND-CPC Adsorbent. XPS spectral analyses of ND-CPC after the Pb(II) uptake are shown in Figure S8 (Supporting Information). The survey spectrum (Figure S8A) shows, in addition to C 1s, N 1s, and O 1s electrons, a new peak at 143 eV confirming the presence of Pb(II) on the surface of ND-CPC. The high-resolution spectrum of Pb 4f electrons in ND-CPC after the Pb(II) uptake shows two peaks at 138.5 and 143.4 eV assigned to the Pb 4f_{7/2} and Pb 4f_{5/2} electrons, respectively, with a spin—orbital splitting of 4.9 eV.³³ These values show a shift to higher binding energies compared to free

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Scheme 2. Proposed Mechanisms for the Adsorption of the Pb(II) and Cr(VI) Ions on ND-CPC

Pb(II) ions, which could be attributed to the formation of complexes with the O and N functional groups on the surface of ND-CPC such as the (COO)₂Pb, COO-Pb⁺, (C-N= $C-)_2Pb$, and $(C-N=C)-Pb^+$ complexes. The complex formation is also confirmed by the high-resolution N 1s and O 1s spectra before and after the adsorption of Pb(II), as shown in Figure S8C,D, respectively. For N 1s after lead adsorption, the electron binding energies are shifted to lower energies because of the strong coordination of the N functional groups such as pyridinic and pyrrolic nitrogen with the acidic lead ions or the graphitic nitrogen with the lone pair of electrons which prefer to interact with Pb(II) by cation $-\pi$ interactions.^{29,34} Similarly, the O 1s high-resolution spectra before and after Pb(II) adsorption (Figure S8E,F, respectively) confirm the complexation between the lead ions and the oxygen functional groups of ND-CPC.^{29,34}

Figure S9A (Supporting Information) shows the XPS survey spectrum of ND-CPC after Cr(VI) adsorption, and it is clear that a new peak appears at 575 eV, indicating the presence of Cr(VI) on ND-CPC. The high-resolution XPS spectrum of Cr on the ND-CPC in Figure S9B shows broad peaks at binding energies of around 586.5 and 576.6 eV, which are assigned to Cr $2p_{1/2}$ and Cr $2p_{3/2}$, respectively. The Cr $2p_{3/2}$ peak is deconvoluted into two peaks at 576.3 and 588.0 eV assigned to Cr(III) in Cr_2O_3 and Cr(VI) in CrO_3 , respectively.³⁵ The presence of Cr(VI) is explained by the electrostatic interaction between chromium anions and the protonated functional groups on the surface of ND-CPC. For example, at low pH, the surface charge of ND-CPC will be positive because of the protonation of its functional groups $(-COOH_2^+, -C-N^+H=$ $C-, -C-N^+H-C-, -C_3-N^+H, -C-N^+OH=C-)$, while Cr(VI) at low pH exists as HCrO₄⁻ anions which are electrostatically attracted to the protonated species on the

surface, leading to the extraction of Cr(VI) ions from the solution. The presence of Cr(III) indicates that Cr(VI) was reduced to Cr(III) by electron-rich functional groups on the ND-CPC. This could be explained by the adsorption of HCrO₄⁻ ions on the protonated functional groups on ND-CPC. This is followed by the transfer of protons to the solution leading to the regeneration of Lewis basic functional groups which will extract Cr(III) from the solution by complexation.^{36,37}

The removal of Cr(VI) by the sequential electrostatic interaction, reduction, and complexation mechanisms is confirmed by the N 1s and O 1s XPS spectra of ND-CPC before and after Cr(VI) adsorption as shown in Figure S9C–F, respectively. Both the O 1s and N 1s spectra after chromium adsorption are deconvoluted to the exact same components as before the removal experiments with significant shifts in binding energies and changes in peak intensities, indicating that these functional groups are involved in the removal of Cr(VI) from the solution.

Scheme 2 illustrates possible mechanisms for the Pb(II) and Cr(VI) adsorption on the ND-CPC adsorbent. Based on the functional groups on the surface of the adsorbent (carboxylic acid-COOH, pyridinic-N, pyrrolic-N, graphitic-N, and pyridine oxide $-N^+-O^-$), uptake of metal ions can be achieved by either physical or chemical interactions. In physical interactions, removal of metal ions can occur through electrostatic interaction or cation $-\pi$ -interaction because of the difference between the surface charge of the adsorbent and the type of ionic species in solution. However, in chemical interactions, removal of metal ions relies on forming coordination bonds between the functional groups of ND-CPC and the metal ions. Also, chemical interactions can occur through redox reactions between metal ions and functional groups on the surface.^{29,38}

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Figure 6. Removal efficiency of metal ions on the ND-CPC adsorbent from a mixture containing Pb(II), Hg(II), Cu(II), Zn(II), Cd(II), and Ni(II) at (A) $C_0 = 10 \text{ mg/L}$ and (B) $C_0 = 250 \text{ mg/L}$ [adsorbent dose = 0.005 g/5 mL, pH 6, T = 298 K, and time = 4 h].

3.5. Effect of Competitive lons. The selectivity of the ND-CPC adsorbent for Pb(II) ions was evaluated in a mixture containing Pb(II), Cu(II), Hg(II), Cd(II), Ni(II), and Zn(II) ions at two different concentrations of 10 and 250 ppm. Figure 6 and Tables S6 and S7 (Supporting Information) show that the removal efficiency for Pb(II) is higher than that of any other ion in the mixture at both the low and high concentrations uptake. At the low concentration of 10 ppm, the removal efficiency is 100% for Pb(II), 96% for Hg(II), 91% for Cu(II), 82% for Zn(II), 25% for Cd(II), and 13% for Ni(II), while at the high concentration of 250 ppm the removal efficiencies for Pb(II) and Hg(II) are 83 and 63%, respectively, compared to 24% for Cu(II) and less than 10% for Zn(II), Cd(II), and Ni(II) ions. Hence, the ND-CPC adsorbent has a superior selectivity for Pb(II) ions from the solution containing a mixture of metal ions. The high selectivity for Pb(II) can be explained by the nature of the Pb ions which are classified as borderline acid, while the pyridinic sites on ND-CPC are classified as borderline bases, and therefore, it is expected that lead ions would form more stable complexes with the ND-CPC pyridinic active sites than other metal ions in the solution.^{29,3}

3.6. Desorption Studies from the Surface of ND-CPC and **Recyclability**. The ability to remove the adsorbed heavy metal ions from the surface of ND-CPC to regenerate the adsorbent is an important requirement for large-scale applications and the development of economically feasible wastewater treatment. Desorption of toxic metals from the ND-CPC adsorbent depends on the type of ionic species and on the surface active sites of the adsorbent. For example, as illustrated in Scheme 2, if the ionic species are in a cationic form such as Pb²⁺, Hg²⁺, or Cd²⁺, they can be desorbed from the surface by acids, and if they are in an anionic form such as $HCrO_4^-$ or $H_2AsO_4^-$, they can be desorbed by bases. Desorption studies from the ND-CPC surface were conducted for Pb(II) and Cr(VI) as examples for cationic and anionic species, respectively. The desorption efficiencies using different concentrations of nitric acid for the recovery of Pb(II) ions or sodium hydroxide for the recovery of Cr(VI) ions from the metal-loaded ND-CPC adsorbents are summarized in Tables S8 and S9, respectively (Supporting Information). The desorption of Pb(II) ions increases from 53.9 to 99.1% when the acidity of the solution increases from 0.1 to 1.0 M. Similarly, the desorption of Cr(VI) ions increases from 50.8 to 99.0% when the basicity of the solution increases from 0.1 to 1.0 M. These results demonstrate that the ND-CPC adsorbent has a high potential for low-cost removal of toxic metal ions

from wastewater because it can be used and recovered several times without significant loss in the adsorption capacity. Figure S10 (Supporting Information) shows the recycling of the ND-CPC adsorbent for Pb(II) ions using 1 M HNO₃. It is clear that after four adsorption—desorption cycles, the adsorption uptake remains above 90% with no significant loss in the adsorption capacity. Therefore, the ND-CPC adsorbent is an efficient and cost-effective adsorbent for the removal of heavy metals from industrial wastewater.

3.7. Comparison of ND-CPC with Other Adsorbents. Finally, it should be noted that the developed ND-CPC adsorbent exhibits one of the highest maximum adsorption capacity (q_{max}) of Pb(II) ions reported in the literature for a variety of organic, inorganic, hybrid, and metal-organic framework (MOF) adsorbents.^{18,31,33,34,39-59} Table S10 (Supporting Information) compares the values of q_{max} of Pb(II) ions measured at comparable experimental conditions by several adsorbents developed in the literature.⁴¹⁻⁵³ It is clear that the removal capacity for lead ions by the ND-CPC $(721 \pm 14 \text{ mg/g})$ adsorbent is higher than most of the reported values by other adsorbents such as thiol-functionalized mesoporous silica (91.5 mg/g),⁴¹ calcium alginate/ graphene oxide (GO) composite aerogel (368 mg/g),⁴² polymer-based ZrP (398 mg/g),43 and GO-ZrP (363 mg/ g).⁴⁴ Additionally, the q_{max} of ND-CPC is also higher than those of functionalized MOF adsorbents such as MOFpolydopamine composite (394.0 mg/g),⁴⁵ NH₂-functionalized Zr-MOF (177 mg/g),⁴⁶ UiO-66-NHC(S)NHMe (232.0 mg/ g),⁴⁷ UiO-66-EDTA (357.9 mg/g),⁴⁸ and UiO-66-amino-thiouracil (386.9 mg/g).⁴⁹ The q_{max} of ND-CPC is also higher than the best graphene-based adsorbents for Pb(II) removal such as chitosan-functionalized GO (556.2 mg/g),⁵⁰ GOwrapped melamine sponge (349.7 mg/g),⁵¹ and threedimensional-graphene/ δ -MnO₂ aerogels (643.6 mg/g).⁵² Although the sulfur-functionalized porous lignin adsorbent exhibits a higher $q_{\text{max}} (952.0 \text{ mg/g})^{53}$ than ND-CPC (721 mg/ g), this adsorbent requires 300 min to reach this high capacity, while the ND-CPC requires only 100 min to achieve the maximum capacity. Moreover, the synthesis of the sulfurfunctionalized lignin adsorbent involves complicated modifications with long processing time unlike the synthesis of ND-CPC which requires only 2 h under mild reaction conditions. Therefore, the ND-CPC adsorbent is clearly among the very top-performing adsorbents reported in the literature for lead removal from contaminated industrial and wastewater.³⁹⁻⁵⁹

4. CONCLUSIONS AND OUTLOOKS

A novel chelating adsorbent, ND-CPC, is developed for the effective removal of Pb(II), Hg(II), and Cr(VI) ions from contaminated water sources. The ND-CPC adsorbent combines multifunctional binding sites including four different nitrogen functional groups (graphitic, pyrrolic, pyridinic, and pyridine oxide) and carboxylic acid functional groups within a high surface area of 1135 m^2/g of the porous carbon structure. The ND-CPC adsorbent shows exceptionally high adsorption affinity for Pb(II) with a capacity of 721 mg/g at pH 6 which is considered among the highest values reported for the removal of Pb(II) ions from water by carbon-based materials. The sorption capacities of 257 and 104 mg/g for Hg(II) and Cr(VI), respectively, are also among the very high uptake values reported for carbon-based adsorbents. The high adsorption capacity is also coupled with fast kinetics where the equilibrium times required for the 100% removal of Pb(II)from 50 ppb and 10 ppm concentrations are 30 s and 60 min, respectively. Even with the very high concentration of 700 ppm, 74% uptake of Pb(II) is achieved within 90 min. The removal efficiency from a mixture of six metal ions at a concentration of 10 ppm is 100% for Pb(II), 96% for Hg(II), 91% for Cu(II), 82% for Zn(II), 25% for Cd(II), and 13% for Ni(II). Regeneration of the ND-CPC adsorbent shows excellent desorption capacities of 99 and 95% for Pb(II) and Cr(VI) ions, respectively. Because of the fast adsorption kinetics, high removal capacity and excellent regeneration, stability, and reusability, the ND-CPC is proposed as a top performing remediation adsorbent for the solid-phase extraction of Pb(II), Hg(II), and Cr(VI) from contaminated water.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c04695.

C 1s, N 1s, and O 1s XPS spectra of ND-PC; N₂ adsorption-desorption isotherms and pore volume distributions of MF-R, ND-PC, and ND-CPC; SEM and TEM images of MF-R; SEM and TEM images of ND-PC; EDX elemental weight % distributions on the surface of ND-CPC; comparison of the Pb(II) removal efficiencies of MF-R, ND-PC, and ND-CPC adsorbents; Langmuir isotherms and pseudo-second order kinetics for the adsorption of Pb(II), Hg(II), Cu(II), Cd(II), Cr(VI), and As(V) ions on ND-CPC; SEM and EDX analysis of the surface of ND-CPC before and after the adsorption of Pb(II) ions; N 1s, O 1s, and Pb 4f XPS spectra of ND-CPC before and after Pb(II) adsorption; Cr 2p, Cr 4f, N 1s, and O 1s XPS spectra of ND-CPC after Cr(VI) adsorption; and recycling of ND-CPC for Pb(II) adsorption; atomic % composition of ND-PC and ND-CPC from XPS analysis; specific surface area and pore size distribution of MF-R, ND-PC, and ND-CPC; Langmuir isotherm parameters for the adsorption of Pb(II) on MF-R, ND-PC, and ND-CPC; Langmuir isotherm parameters for the adsorption of Pb(II), Hg(II), Cr(VI), Cd(II), Cu(II), and As(V) ions on ND-CPC; kinetic parameters for adsorption of Pb(II), Hg(II), Cr(VI), Cd(II), Cu(II), and As(V) ions on the ND-CPC; adsorption capacities of ND-CPC in mixed metal ion systems with 10 ppm and 250 ppm concentrations; desorption study of Pb(II) from ND-

CPC; desorption study of Cr(VI) from ND-CPC; and comparison of adsorption capacity of Pb(II) by several adsorbents (PDF)

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Notes

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