

Research Article

Effects of Nanoscale Carbon Black Modified by HNO_3 on Immobilization and Phytoavailability of Ni in Contaminated Soil

Jiemin Cheng, Lei Yu, Tong Li, Yuzhen Liu, Chengxiu Lu, Tingting Li, and Hanwei Wang

College of Population Resources and Environment, Shandong Normal University, Jinan 250014, China

Correspondence should be addressed to Jiemin Cheng; 1756736835@qq.com

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A surface-modified nanoscale carbon black (MCB) as Ni adsorbent in contaminated soil was prepared by oxidizing the carbon black with 65% HNO_3 . The surface properties of the adsorbent were characterized by zeta potential analysis, scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIRs). Batch experiments were conducted to evaluate the improvement of Ni^{2+} adsorption by MCB. Greenhouse cultivation experiments were conducted to examine the effect of MCB on the DTPA-extractable Ni^{2+} in soil, Ni^{2+} uptake of ryegrass shoot, and growth of ryegrass. Results indicated that MCB had much lower negative zeta potential, more functional groups for exchange and complexation of cation, and more heterogeneous pores and cavities for the adsorption of cation than the unmodified parent one (CB). MCB showed enhanced sorption capacity for Ni ($q_{\text{max}}, 49.02 \text{ mg}\cdot\text{g}^{-1}$) compared with CB ($q_{\text{max}}, 39.22 \text{ mg}\cdot\text{g}^{-1}$). Greenhouse cultivation experiment results showed that the biomass of ryegrass shoot and the Ni uptake of the ryegrass shoot were significantly increased and the concentrations of DTPA-extractable Ni in soil were significantly decreased with the increasing of MCB amount. It is clear from this work that the MCB had good adsorption properties for the Ni and could be applied in the in situ immobilization and remediation of heavy metal contaminated saline-alkali soils.

1. Introduction

Heavy metal pollution is a serious environmental problem. Refineries, mines, and fertilizers (exclusively phosphate) are the major sources of Ni dispersion in soil [1]. Nearly all the concentrations of Ni are higher than their background values of soil in some areas in China [2]. Due to the potential public health risk associated with intake, Ni has been a group of pollutants of much concern. Among the many remediation methods, in situ immobilization remediation successfully demonstrated its superiority for the remediation of farmland contaminated by heavy metals of low concentration [3–5]. The effectiveness of in situ immobilization remediation depends not only on a range of factors such as types of contaminants, reagents, soil conditions, and land use [6] but also on the physicochemical properties of the immobilization materials, so developing efficient, low-cost,

and environment-friendly immobilization materials is a key to successful application of remediation technology for the contaminated soils with lower concentration of heavy metals.

Because the nanoscale carbon black has large specific surface area, highly active adsorption sites, and good electric ability, considerable attention has been focused on developing and applying it in wastewater treatment [7, 8] and in situ immobilization remediation of contaminated soil [9, 10]. The nanoscale carbon black is a hydrophobic and nonpolar adsorbent, and it has strong adsorption ability to nonpolar organic compounds [11–15]. However, the nanoscale carbon black has poor adherence to heavy metal ions. In fact, research has shown that the maximum amounts of Pb(II) adsorption by the nanoscale carbon black were lower than expandable clay mineral and humic acid [16, 17]. Surface modification of the nanoscale carbon black by appropriate physical and chemical treatments could improve its adsorption capacities for heavy

metal ions [18]. The adsorption quantities of Cu(II) or Cd(II) on a surface-modified nanoscale carbon black oxidized with 65% HNO_3 were significantly increased [19, 20]. It had been found that the surface-modified nanoscale carbon black significantly reduced the bioavailability of Cu and Zn in red earth with lower pH (3.99) [21, 22]. When the surface-modified nanoscale carbon was added into acidic soil, the pH value of soil increased, and then the bioavailability of heavy metals in soil was reduced. After treating with acid, the nanoscale carbon black has a pH value of about 5.5, but its effect in higher pH saline-alkali soil (7.76) is unknown.

The major objective of the present study is to compare the surface properties and the adsorption capacity between a surface-modified nanoscale carbon black (MCB) and the unmodified parent one (CB) by batch experiment and to investigate the feasibility of using the modified nanoscale carbon black as immobilization material for Ni-contaminated saline-alkali soil by cultivation experiment. This work provided a proof for an application of the MCB in in situ immobilization remediation of metals contaminated saline-alkali soils.

2. Materials and Methods

2.1. Modification of Nanoscale Carbon Black. A commercial nanoscale carbon black (CB) with particle size of 20–70 nm was purchased from Jinan Carbon Black Factory, Shandong Province, China. This carbon black was further oxidized with 65% HNO_3 for modification by refluxing 10 g of carbon black with 150 mL HNO_3 (65%) in a conical flask at 110°C for 2 h. The modified nanoscale carbon black (MCB) was filtered, washed with deionized water until the pH of the filtrate became stable (pH is about 5.5), and finally dried in a vacuum oven at 110°C for 24 h [19].

2.2. Surface Properties

2.2.1. Zeta Potential of the CB or MCB. The CB and MCB suspensions ($0.4\text{ g}\cdot\text{L}^{-1}$) containing 0.01 M NaNO_3 as background electrolyte were prepared at different pH values. The suspensions were dispersed ultrasonically at a frequency of 40 kHz and a power of 300 W for 1 h and then shaken for 20 h at 25°C . After being equilibrated for two days, the zeta potential was measured using a JS94G+ microelectrophoresis instrument (Shanghai Zhongchen Digital Technique Equipment Ltd. Co., Shanghai, China) and the suspension pH was also determined.

2.2.2. Fourier Transform Infrared Spectroscopy (FTIRs) of the CB or MCB. Infrared spectra (IR) of the CB or MCB were recorded using a Perkin-Elmer 2000 Fourier transform infrared spectroscopy (FTIRs) spectrometer fitted with a deuterated triglycine sulfate (DTGS) detector covering the frequency range of $500\text{--}4000\text{ cm}^{-1}$. The sample cell was purged with nitrogen gas throughout data collection to exclude carbon dioxide and water vapor. Ten milligrams of the dried samples was evenly dispersed in 200 mg of spectroscopic grade KBr to record the spectra.

2.2.3. SEM (Scanning Electron Microscopy) of the CB or MCB. The samples were placed on the exposed upper surface of double-sided carbon tape attached to standard AL mounting stubs. The SEM analyses were carried out using a LEO 982 field-emission SEM with an Oxford energy dispersive X-ray analyzer.

2.3. Batch Adsorption Experiments

2.3.1. Adsorption Kinetics Experiments. Ni adsorption kinetics experiments were conducted by mixing the suspensions containing 0.1000 g CB or MCB, 30 mL Ni standard solution ($180\text{ mg Ni}^{2+}\cdot\text{L}^{-1}$), and 0.01 M NaCl as electrolyte in 12 PTFE centrifuge tubes. Tubes were sealed and shaken at the temperature of 25°C for 20 min, 30 min, 40 min, 60 min, 90 min, 120 min, 180 min, 300 min, 420 min, 600 min, 720 min, and 900 min. Finally, the amount of Ni^{2+} was determined after centrifuging and filtering through $0.45\ \mu\text{m}$ membrane. In the meantime, the controlled experiments were carried out by the same procedure as above except utilizing the CB instead of MCB. Both experiments of MCB and CB were performed in duplicate. Kinetic curves of the adsorption were made at last. The residual Ni^{2+} concentration in solution samples was measured using an atomic absorption spectrometry (Thermo Orion 9609 BN) according to the standard method [23].

2.3.2. Adsorption Isotherms Experiments. The adsorption isotherms were obtained by mixing the suspensions, containing 0.1000 g CB or MCB, 30 mL Ni standard solution (0, 20, 40, 60, 80, 100, 120, 150, and $180\text{ mg Ni}^{2+}\cdot\text{L}^{-1}$), and 0.01 M NaCl as electrolyte in 50 mL PTFE (polytetrafluoroethylene) centrifuge tubes. Tubes were sealed and shaken at the temperature of 25°C for 2 h. Finally, the amount of Ni^{2+} was determined after centrifuging and filtering through $0.45\ \mu\text{m}$ membrane. In the meantime, the controlled experiments were carried out by the same procedure as above except utilizing the CB instead of MCB. Adsorption isotherms for the adsorption were made at last.

2.4. Greenhouse Experiments

2.4.1. Collection of Soil Samples and Preparation. A saline-alkali soil of plough layers (0–20 cm) was sampled from Dongying (Shandong Province, China). The saline-alkali soil used in the research is from the Yellow River alluvial parent material. The soil sample was air-dried and sieved (2 mm mesh). The general properties of the soil were pH 7.76, salt content 0.35%, cation exchange capacity (CEC) $9.29\text{ cmol}\cdot\text{kg}^{-1}$, organic matter (OM) $8.34\text{ g}\cdot\text{kg}^{-1}$, clay content up to 18.5%, Yellow River alluvial parent materials, Ni $22.61\text{ mg}\cdot\text{kg}^{-1}$, and Cd $0.49\text{ mg}\cdot\text{kg}^{-1}$.

The following properties were analyzed: pH (by CaCl_2 extraction), organic matter (by $\text{H}_2\text{SO}_4\text{-K}_2\text{Cr}_2\text{O}_7$ with external heating), CEC (by Kjeldahl digestion), available Ni (extracted by DTPA, pH 7.3), and total Ni (by $\text{HNO}_3\text{-HClO}_4\text{-HF}$ extraction), followed by atomic absorption spectrophotometry (AAS) [24].

2.4.2. Experimental Design and Procedures. The soil environmental quality standards value of China for Ni in a saline-alkali soil is lower than $60 \text{ mg}\cdot\text{kg}^{-1}$ [25]. The soil background value of Ni is about $22.61 \text{ mg}\cdot\text{kg}^{-1}$ in the investigation area of this paper, and the Ni content in contaminated soil ranged from $80 \text{ mg}\cdot\text{kg}^{-1}$ to $100 \text{ mg}\cdot\text{kg}^{-1}$.

Ni^{2+} was added to soil and amended to contain $100 \text{ mg Ni kg}^{-1}$ by adding appropriate concentrations of $\text{Ni}(\text{NO}_3)_2$. Deionised water was added to the soils to achieve a moisture content of 70% of field capacity. To ensure even dispersion of Ni, soils were thoroughly mixed while adding $\text{Ni}(\text{NO}_3)_2$ and water. The soils were incubated at room temperature (at about 20°C) for 2 months, allowing Ni^{2+} to be distributed into various fractions. During the period, soil moisture content was carefully monitored.

The MCB of 0, 0.5%, and 1% was added into soil, mixed thoroughly, and placed into pots (1.5 kg per pot). For each pot, 0.33 g urea and 0.35 g K_2HPO_4 were added as fertilizer and mixed thoroughly. There were three replicates for each treatment, with 9 pots in total. All pots were adjusted regularly to 70% of field water-holding capacity using deionized water.

Fifteen well-germinated ryegrass seeds (*Lolium multiflorum*) (obtained from the College of Life Sciences, Shandong Normal University, China) were sowed in each pot. The pots were placed in the greenhouse under a random block design and the ryegrass shoot was harvested after 60 days (approximately 0.5 cm aboveground), and the shoot was separated, washed, and weighed after adhering water was removed with filter paper. The ryegrass shoot was digested by $\text{HCl-HNO}_3\text{-HClO}_4$, and Ni was determined by AAS [24]. The soil subsamples were air-dried and ground to pass through a 1-mm sieve before use.

2.5. Statistical Methods. Arithmetic means and standard errors of the mean were calculated using Microsoft Excel *t*-test (unequal variance assumed to be $P < 0.05$ was used to determine the difference between treatments with and without MBC) [26].

3. Results and Discussion

3.1. Surface Characteristics of CB and MCB

3.1.1. The Zeta Potential of the CB and MCB. The zeta potentials of both CB and MCB were shown in Figure 1. MCB has more negative charge than CB, and the zeta potential decreased from -20 mV to -60 mV from pH 3 to 8. Zeta potential is widely used to quantify the magnitude of the electrical charge in the double layer [27]. The MCB particles had lower zeta potential values than the CB particles at the same pH and should have higher adsorption affinity for Ni^{2+} than CB.

3.1.2. The FTIRs of the CB or MCB. The FTIRs analyses were conducted to identify characteristic functional groups. The IR spectra of CB and MCB were presented in Figure 2. Compared with CB, MCB exhibited some characteristic peaks at wavenumbers of 1580, 1709, and 3424 cm^{-1} , which

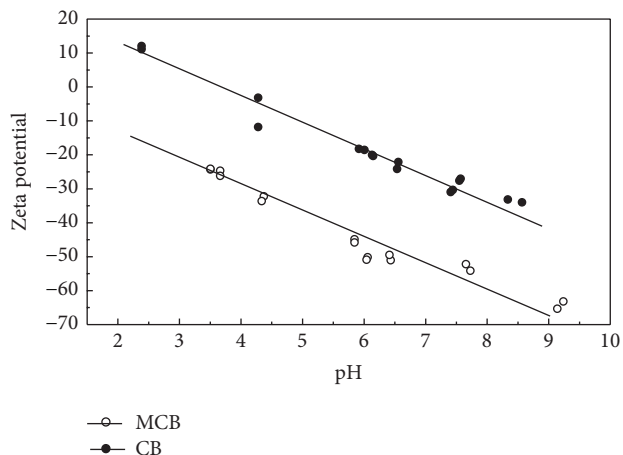


FIGURE 1: Zeta potential of MCB and CB.

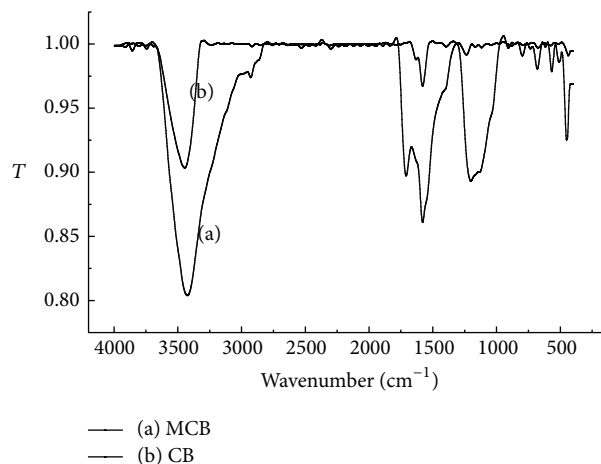


FIGURE 2: Infrared spectrum of MCB and CB.

were associated with hydroxyl groups or carbonyl groups, carboxylic acids, and hydroxyl groups [28], respectively. As it can be seen from Figure 2, the absorption of phenol hydroxyl C-O, which is at wavenumbers of 1250 cm^{-1} , was increased compared with CB. The increased amounts of these functional groups resulted in the increasing surface cation exchange and complexation capacity of MCB [29].

3.1.3. The SEMs of CB or MCB. Figure 3 showed SEM images of CB and MCB. The pore structure had not been observed from the SEM image of CB and exhibited nonadhesive appearance and formation of agglomerates. Fusing of aggregates by van der Waals forces resulted in the formation of new structures—agglomerates, as previously described in the literature [30]. Comparing with CB, MCB particles had heterogeneous pores and cavities. CB is produced by partial combustion of petroleum or natural gas, and its pH is normally neutral to basic (pH from 6.2 to 9.6), depending on the feedstock and pyrolysis conditions used in various studies [31, 32]. The CB surfaces morphology change depends on the different treating methods. For example, the acetic

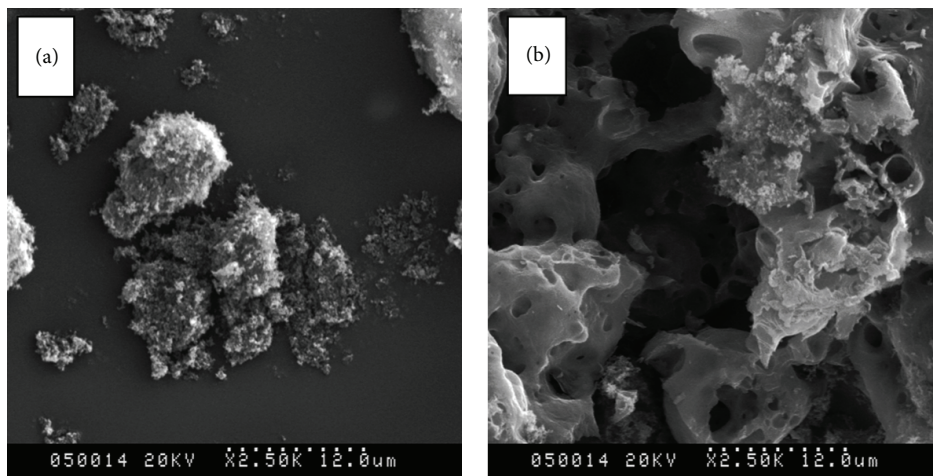


FIGURE 3: (a) SEM image of CB. (b) SEM image of MCB.

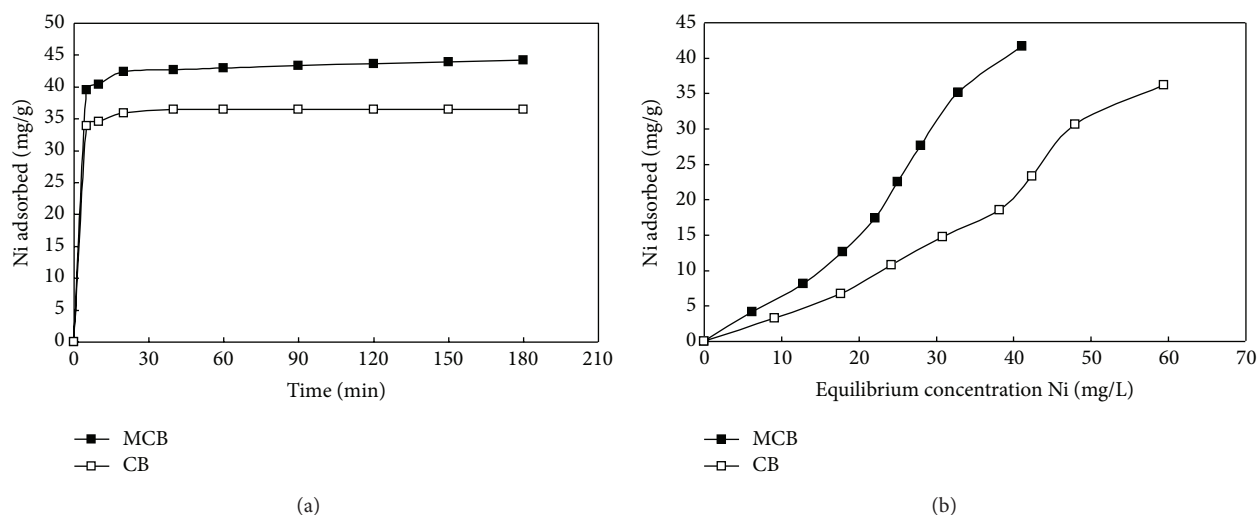


FIGURE 4: Adsorption kinetics (a) and adsorption isotherms (b) of Ni on MCB and CB at pH = 7.0 and $T = 25^{\circ}\text{C}$.

acid modification reduces the number of cracks and pores on CB surfaces, which are clogged by adsorbed acetic acid [33]. Therefore, selecting an appropriate acid is crucial. In our study, after treating with nitric acid, pores and caves formed on the MCB surface. Those pores and caves provided larger exposed surface area for the adsorption of cation.

3.2. Adsorption Kinetics and

Adsorption Isotherms of CB or MCB

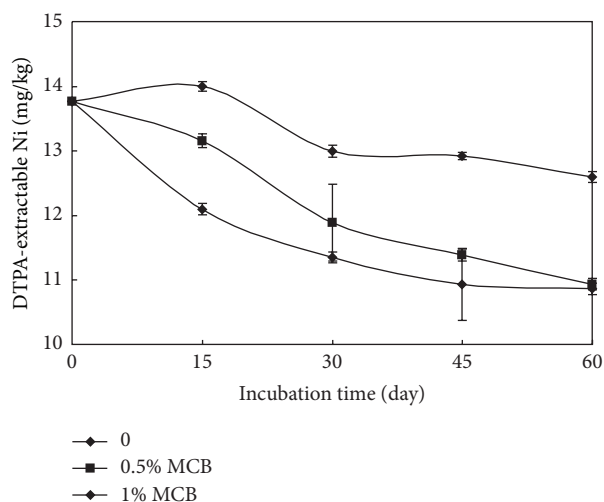
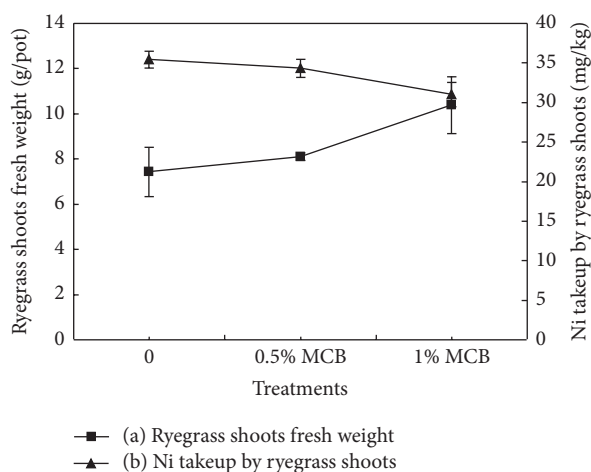
3.2.1. Adsorption Kinetics. Figure 4(a) showed the adsorption kinetic curves of Ni on CB and MCB at pH 7.0. Ni adsorbed by CB or MCB occurred rapidly and reached equilibrium within about 20 minutes. The pseudo-first-order kinetic equation [34] and pseudo-second-order kinetic equation [35] were applied to fit the adsorption kinetic data in Figure 4(a).

It is clear from Table 1, and the pseudo-first-order model did not adequately fit the experimental data because all

the R^2 of CB or MCB is 0.5077 or 0.6919. However, the pseudo-second-order model for adsorption of Ni onto CB or MCB agrees well with experimental data because all values of R^2 are greater than 0.999. Liu and Cheng [20] reported that the adsorption kinetic model of Cu^{2+} and Cd^{2+} on CB or MCB followed pseudo-second-order model well. In general, the pseudo-second-order rate expression was used to describe chemisorption involving valency forces through the sharing or exchange of electrons between the adsorbent and adsorbate as covalent forces and ion exchange [36]. The much lower rate of constant k_2 for MCB (i.e., 0.01799) than for CB (i.e., 0.1532) also indicated the much faster adsorption kinetics of Ni^{2+} on CB than on MCB. It could be ascribed to more heterogeneous pores and cavities on the MCB particles than CB (Figure 3) [19]. The rate of Ni^{2+} into internal surface sites of the CB or MCB was slower than on external surface sites. In most cases, the pseudo-second-order chemical reaction kinetics provide the best

TABLE 1: The best-fit model parameters for adsorption of Ni²⁺ on CB and MCB.

Sorbents	Pseudo-first-order model			Pseudo-second-order model			Langmuir isotherm			Freundlich isotherm		
	q_{1e} (mg/g)	k_1 (min ⁻¹)	R_1^2	q_{2e} (mg/g)	k_2 (g/(mg·min))	R_2^2	q_{max} (mg/g)	K_L (L·kg ⁻¹)	R^2	K_F (mg/g)	n	R^2
CB	1.220	0.1101	0.5077	36.49	0.1532	0.9999	39.22	0.008901	0.9205	6.104	0.7576	0.9823
MCB	3.032	0.1010	0.6919	44.25	0.01799	0.9999	49.02	0.01200	0.8272	2.934	0.7740	0.9926

FIGURE 5: Effect of MCB on DTPA-extractable Ni in soil. Ni²⁺ was added to soil at the ratio of 100 mg·kg⁻¹ and the MCB was added at the ratio of 0, 0.5%, and 1%, respectively.FIGURE 6: Effect of MCB on the biomass of ryegrass shoots and Ni uptake by ryegrass shoots. Ni²⁺ was added to soil at the ratio of 100 mg·kg⁻¹ and the MCB was added at the ratio of 0, 0.5%, and 1%, respectively.

correlation of the experimental data, whereas the pseudo-first-order model proposed fits the experimental data well for an initial period of the first reaction step only [37]. Cheng et al. [38] reported that the adsorption of Cu²⁺ or Cd²⁺ on MCB reached equilibrium rapidly within 30 minutes and more than 90% of the equilibrium adsorption amount.

3.2.2. *Adsorption Isotherms.* Figure 4(b) illustrated the adsorption isotherms of Ni²⁺ on the CB and MCB at pH 7.0. The *Freundlich* isotherm and *Langmuir* isotherm were applied to fit the adsorption isotherm data.

The best-fit parameters are listed in Table 1. The R^2 values suggested that the *Freundlich* isotherm described the adsorption data better than the *Langmuir* isotherm. The value of q_{max} (maximum adsorption capacity) for CB was 39.22 mg·g⁻¹, and for MCB it was 49.02 mg·g⁻¹. Literature data confirm that the affinity of the carboxylic functional groups for metal ions is very high [39], so the increase of adsorbed capacity might be attributed to the increase of oxygenic functional groups and the consequent increase of surface cation exchange and complexation capacity of the MCB [29]. It is consistent with the conclusion that oxidation increased the functional groups on CB surfaces and then increased the maximum adsorption capacity of heavy metals. Various methods such as acid treatment, base treatment, impregnation treatment, ozone treatment, surfactant treatment, plasma treatment, and microwave treatment have been studied to develop surface-modified activated carbons [40]. Ankica and Jadranka results showed that modification by acetic acid increases the adsorption capacity of carbon black from 18.3823 to 86.9566 mg Ni(II) g⁻¹, though the specific surface area of carbon black is decreased, and its surface becomes more homogeneous after modification [33]. The Ni adsorption capacity on microwave and thermally heated activated carbon was 12.00 and 8.42 mg·g⁻¹, respectively [41]. The q_{max} is different in different modification methods, so it is necessary to further study the adsorption mechanism of CB modified by different methods.

3.3. Effect of MCB on Available Ni²⁺ in Soil

3.3.1. *DTPA-Extractable Ni in Soil.* The DTPA (diethylene triamine pentaacetic acid) extraction method has been employed well to estimate the metal availability for plants in neutral to calcareous soils [42]. The concentrations of DTPA-extractable Ni in soils were significantly decreased with the increase of incubation day, when Ni²⁺ was added to soil at the ratio of 100 mg·kg⁻¹ and the MCB was added at the ratio of 0, 0.5%, and 1%, respectively (Figure 5). Compared with non-MCB, the concentrations of DTPA-Ni decreased by 12.15% and 13.58% when the MCB was added at ratios of 0.5% and 1% at 15 days ($P < 0.05$) and decreased by 13.18% and 13.74% at 60 days. Cui et al. [43] study showed that CB amendment offers a basic option to reduce Cd and Pb bioavailability and change the fractions, when the CB was applied at rates of 0, 10, 20, and 40 tons per hectare. Cheng et al. [22] study showed

that the concentrations of DTPA-extractable Cu and Zn in soil were significantly decreased by addition of MCB.

Notably, the results mentioned above were obtained in lower pH, but the effects of MCB on the bioavailability were obtained in higher pH saline-alkali soil in this paper. pH of biochar is normally neutral to basic (pH from 6.2 to 9.6), depending on the feedstock and pyrolysis conditions used in various studies [31, 32]. When biochar is added in acidic soil, the pH value of soil is increased and then reduces the bioavailability of heavy metals in soil. However, the pH value of MCB is about 5.5, and the pH value of alkaline soil is about 7.8. The mechanism of effect bioavailability of heavy metals in soil may be different between biochar and MCB. The effect mechanism of MCB on the bioavailability of heavy metals in soil may be by adsorption and chelation, because it has lower negative zeta potential [19] and more hydroxyl groups or carboxyl groups, carboxylic acids, and hydroxyl groups [28].

3.3.2. Ryegrass Shoots Biomass and Ni Uptake of Ryegrass Shoots. Adding MCB significantly increased the biomass of ryegrass shoots, and they increased with the increase of MCB added amount, when Ni^{2+} was added to soil at the concentration of $100 \text{ mg}\cdot\text{kg}^{-1}$ and the MCB was added at the ratio of 0, 0.5%, and 1%, respectively (Figure 6). Compared with non-MCB, the MCB groups showed the fresh weight of ryegrass shoots increased by 9.03% and 39.75%, respectively ($P < 0.05$). The Ni uptake of the ryegrass shoots decreased with the increase of the MCB (Figure 6). Compared with non-MCB, the Ni uptake of the ryegrass shoots was not significantly different when the MCB addition was in 0.5% and significantly different ($P < 0.05$) when the MCB addition was in 1% and the Ni uptake of the ryegrass shoots decreased by 12.48%.

Previous works indicated that the concentrations of DTPA-extractable heavy metals in soil were positive linearly correlated with the uptake heavy metals by plant [42]. Méndez et al. [44] suggested that the risk of leaching of Cu, Ni, and Zn was lower in the soil treated with biochar and biochar amended samples also reduced plant availability of Ni, Zn, Cd, and Pb. Application of chicken manure-derived biochar significantly reduced NH_4NO_3 extractable Cd, Cu, and Pb concentrations of soils and increased plant dry biomass by 353 and 572% for shoot and root [45]. Cheng et al. [22] reported that the Cu and Zn uptake of the ryegrass shoots decreased by 34.98% and 14.52% in acid soil, comparing with non-MCB. In this study, the concentrations of DTPA-extractable Ni in soils were significantly decreased with the increment of MCB, and when the MCB addition was in 1%, the Ni uptake by ryegrass shoots decreased. The carbon black modified by this method is a potential application for the in situ immobilization remediation of heavy metal contaminated saline-alkali soil.

4. Conclusions

It is clear from this work that the nanoscale carbon black modified by HNO_3 (MCB) has lower negative zeta potential

than the CB, more functional groups for exchange and complexation of cation and heterogeneous pores and cavities for the adsorption of cation than unmodified CB. The MCB had much higher q_{max} ($49.02 \text{ mg}\cdot\text{g}^{-1}$) of nickel than the CB ($39.22 \text{ mg}\cdot\text{g}^{-1}$) and showed very good adsorption and complexation properties for Ni^{2+} in soil. The MCB could be applied for the in situ immobilization remediation of heavy metal contaminated soils.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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References

- [1] S. P. McGrath, "Chromium and nickel," in *Heavy Metals in Soils*, B. J. Alloway, Ed., pp. 152–178, Blackie, New York, NY, USA, 1995.
- [2] B. Wei and L. Yang, "A review of heavy metal contaminations in urban soils, urban road dusts and agricultural soils from China," *Microchemical Journal*, vol. 94, no. 2, pp. 99–107, 2010.
- [3] T. A. Martin and M. V. Ruby, "Review of *in situ* remediation technologies for lead, zinc, and cadmium in soil," *Remediation Journal*, vol. 14, no. 3, pp. 35–53, 2004.
- [4] M. A. Hashim, S. Mukhopadhyay, J. N. Sahu, and B. Sengupta, "Remediation technologies for heavy metal contaminated groundwater," *Journal of Environmental Management*, vol. 92, no. 10, pp. 2355–2388, 2011.
- [5] Z. Yao, J. Li, H. Xie, and C. Yu, "Review on remediation technologies of soil contaminated by heavy metals," *Procedia Environmental Sciences*, vol. 16, pp. 722–729, 2012.
- [6] M. C. Jung, "Heavy metal concentrations in soils and factors affecting metal uptake by plants in the vicinity of a Korean Cu-W mine," *Sensors*, vol. 8, no. 4, pp. 2413–2423, 2008.
- [7] C. Wu, X. Zhang, and G. Li, "Sorption of Hg^{2+} , As^{3+} , Pb^{2+} and Cd^{2+} by black carbon," *Journal of Agro-Environment Science*, vol. 26, no. 2, pp. 770–774, 2007.
- [8] B. Gong, Y. Qiu, Y. Zhao, and M. Huang, "Laboratory study on adsorption of methylene blue on black carbon in aqueous solution," *Environmental Science & Technology (China)*, vol. 32, no. 11, pp. 18–23, 2009 (Chinese).
- [9] L. Beesley, E. Moreno-Jiménez, J. L. Gomez-Eyles, E. Harris, B. Robinson, and T. Sizmur, "A review of biochars' potential role in the remediation, revegetation and restoration of contaminated soils," *Environmental Pollution*, vol. 159, no. 12, pp. 3269–3282, 2011.
- [10] J. Paz-Ferreiro, H. Lu, S. Fu, A. Méndez, and G. Gascó, "Use of phytoremediation and biochar to remediate heavy metal polluted soils: a review," *Solid Earth*, vol. 5, no. 1, pp. 65–75, 2014.
- [11] M. T. O. Jonker and A. A. Koelmans, "Sorption of polycyclic aromatic hydrocarbons and polychlorinated biphenyls to soot

- and soot-like materials in the aqueous environment: mechanistic considerations," *Environmental Science and Technology*, vol. 36, no. 17, pp. 3725–3734, 2002.
- [12] H. Bärning, T. D. Bucheli, D. Broman, and Ö. Gustafsson, "Soot-water distribution coefficients for polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans and polybrominated diphenylethers determined with the soot cosolvency-column method," *Chemosphere*, vol. 49, no. 6, pp. 515–523, 2002.
- [13] G. Cornelissen and Ö. Gustafsson, "Sorption of phenanthrene to environmental black carbon in sediment with and without organic matter and native sorbates," *Environmental Science and Technology*, vol. 38, no. 1, pp. 148–155, 2004.
- [14] X.-Y. Yu, G.-G. Ying, and R. S. Kookana, "Sorption and desorption behaviors of diuron in soils amended with charcoal," *Journal of Agricultural and Food Chemistry*, vol. 54, no. 22, pp. 8545–8550, 2006.
- [15] S.-L. Wang, Y.-M. Tzou, Y.-H. Lu, and G. Sheng, "Removal of 3-chlorophenol from water using rice-straw-based carbon," *Journal of Hazardous Materials*, vol. 147, no. 1-2, pp. 313–318, 2007.
- [16] K. Guo and Y. Ma, "Research on adsorption and affecting factors of Pb^{2+} on several clay minerals," *Geology/Geochemistry*, vol. 4, pp. 109–113, 1997.
- [17] G. Li, S. Wei, and S. Mou, "Adsorptive characteristics and influence factors of humic acid on lead in soil," *Journal of Agro-Environment Science*, vol. 23, no. 2, pp. 308–312, 2004.
- [18] Y. Fan, B. Wang, and L. Wang, "Surface characteristics of modified carbons and its adsorption performance of heavy metal ions," *Environmental Chemistry*, vol. 20, no. 5, pp. 437–443, 2001 (Chinese).
- [19] D.-M. Zhou, Y.-J. Wang, H.-W. Wang, S.-Q. Wang, and J.-M. Cheng, "Surface-modified nanoscale carbon black used as sorbents for Cu(II) and Cd(II)," *Journal of Hazardous Materials*, vol. 174, no. 1-3, pp. 34–39, 2010.
- [20] Y.-Z. Liu and J.-M. Cheng, "Adsorption kinetics and isotherms of Cu (II) and Cd(II) onto oxidized nano carbon black," *Advanced Materials Research*, vol. 529, pp. 579–584, 2012.
- [21] H.-W. Wang, Y.-J. Wang, J.-H. Chen, S.-Q. Wang, J.-M. Cheng, and D.-M. Zhou, "Application of modified nano-particle black carbon for the remediation of soil heavy metal pollution," *China Environmental Science*, vol. 29, no. 4, pp. 431–436, 2009.
- [22] J.-M. Cheng, Y.-Z. Liu, and H.-W. Wang, "Effects of surface-modified nano-scale carbon black on Cu and Zn fractionations in contaminated soil," *International Journal of Phytoremediation*, vol. 16, no. 1, pp. 86–94, 2014.
- [23] APHA, *Standard Methods*, American Public Health Association, Washington, DC, USA, 19th edition, 1995.
- [24] R. H. Shi, *The Analytical Methods of Soil Agricultural Chemistry*, Chinese Agricultural Press, Beijing, China, 1996.
- [25] SEPA, "Environmental quality standard for soils," GB 15618-1995, State Environmental Protection Administration of the People's Republic of China, Beijing, China, 1995, (Chinese).
- [26] P. Armitage and G. Berry, *Statistical Methods in Medical Research*, Blackwell Scientific Publications, London, UK, 3rd edition, 1994.
- [27] R. J. Hunter, *Zeta Potential in Colloid Science: Principles and Applications*, Academic Press, London, UK, 1981.
- [28] A. Stafiej and K. Pyrzynska, "Adsorption of heavy metal ions with carbon nanotubes," *Separation and Purification Technology*, vol. 58, no. 1, pp. 49–52, 2007.
- [29] Y.-H. Li, J. Ding, Z. K. Luan et al., "Competitive adsorption of Pb^{2+} , Cu^{2+} and Cd^{2+} ions from aqueous solutions by multiwalled carbon nanotubes," *Carbon*, vol. 41, no. 14, pp. 2787–2792, 2003.
- [30] T. C. Gruber, T. W. Zerda, and M. Gerspacher, "Three-dimensional morphology of carbon black aggregates," *Carbon*, vol. 31, no. 7, pp. 1209–1210, 1993.
- [31] F. G. A. Verheijen, S. Jeffery, A. C. Bastos, M. van der Velde, and I. Diafas, "Biochar application to soils—a critical scientific review of effects on soil properties, processes and functions," EUR 24099 EN, Office for the Official Publications of the European Communities, Luxembourg, 2009.
- [32] F. Rees, M. O. Simonnot, and J. L. Morel, "Short-term effects of biochar on soil heavy metal mobility are controlled by intraparticle diffusion and soil pH increase," *European Journal of Soil Science*, vol. 65, no. 1, pp. 149–161, 2014.
- [33] A. Radenović and J. Malina, "Adsorption ability of carbon black for nickel ions uptake from aqueous solution," *Hemjska Industrija*, vol. 67, no. 1, pp. 51–58, 2013.
- [34] S. Lagergren, "About the theory of so-called adsorption of soluble substances," *Kungliga Svenska Vetenskapsakademiens Handlingar*, vol. 24, pp. 1–39, 1898.
- [35] Y. S. Ho and G. McKay, "A comparison of chemisorption kinetic models applied to pollutant removal on various sorbents," *Process Safety and Environmental Protection*, vol. 76, no. 4, pp. 332–340, 1998.
- [36] Y.-S. Ho, "Review of second-order models for adsorption systems," *Journal of Hazardous Materials*, vol. 136, no. 3, pp. 681–689, 2006.
- [37] Y. S. Ho and G. McKay, "Pseudo-second order model for sorption processes," *Process Biochemistry*, vol. 34, no. 5, pp. 451–465, 1999.
- [38] J. Cheng, H. Wang, and D. Zhou, "Adsorption-desorption of Cu^{2+} and Cd^{2+} on the surface of modified nano-scale black carbon," *Res. Environ. Sci.*, vol. 24, no. 12, pp. 1409–1415, 2011 (Chinese).
- [39] D. Mugisidi, A. Rinaldo, J. W. Soedarsono, and M. Hikam, "Modification of activated carbon using sodium acetate and its regeneration using sodium hydroxide for the adsorption of copper from aqueous solution," *Carbon*, vol. 45, no. 5, pp. 1081–1084, 2007.
- [40] A. Bhatnagar, W. Hogland, M. Marques, and M. Sillanpää, "An overview of the modification methods of activated carbon for its water treatment applications," *Chemical Engineering Journal*, vol. 219, pp. 499–511, 2013.
- [41] T. M. Alslaiibi, I. Abustan, M. A. Ahmad, and A. A. Foul, "Microwave irradiated and thermally heated olive stone activated carbon for nickel adsorption from synthetic wastewater: a comparative study," *AIChE Journal*, vol. 60, no. 1, pp. 237–250, 2014.
- [42] L. J. Miles and G. R. Parker, "DTPA soil extractable and plant heavy metal concentrations with soil-added Cd treatments," *Plant and Soil*, vol. 51, no. 1, pp. 59–68, 1979.
- [43] L. Cui, J. Yan, Y. Yang et al., "Influence of biochar on microbial activities of heavy metals contaminated paddy fields," *BioResources*, vol. 8, no. 4, pp. 5536–5548, 2013.
- [44] A. Méndez, A. Gómez, J. Paz-Ferreiro, and G. Gascó, "Effects of sewage sludge biochar on plant metal availability after application to a Mediterranean soil," *Chemosphere*, vol. 89, no. 11, pp. 1354–1359, 2012.
- [45] J. H. Park, G. K. Choppala, N. S. Bolan, J. W. Chung, and T. Chuasavathi, "Biochar reduces the bioavailability and phytotoxicity of heavy metals," *Plant and Soil*, vol. 348, no. 1-2, pp. 439–451, 2011.



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