

## Adsorption Performance of Carbon-Coated Magnetic Nickel Nanoparticles for Methylene Blue [Postprint]

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### Abstract

Core/shell-type carbon-coated nickel nanoparticles (Ni@C NPs) were synthesized in-situ by evaporating bulk metallic nickel using the direct current arc plasma method in a methane atmosphere. A distinct core/shell structure was observed via transmission electron microscopy, consisting of a metallic nickel core coated with a graphitic carbon layer 3-5 nm thick. The BET specific surface area was calculated to be  $38.82 \text{ m}^2 \cdot \text{g}^{-1}$  based on the N<sub>2</sub> adsorption isotherm. Surface modification with hydrogen peroxide was performed to functionalize oxygen-containing groups, which improved carbon surface wettability and hydrophilicity, enabling application as an adsorbent for methylene blue dye. The effects of adsorption time, initial concentration, and pH value on the adsorption capacity were systematically investigated. Kinetics were investigated using pseudo-first-order and pseudo-second-order models, while adsorption isotherms were analyzed via Langmuir and Freundlich model fitting. Five cycles of adsorption-desorption recycling experiments were conducted, after which the powdered adsorbent was collected, demonstrating a recovery rate of 69.4%. Results from magnetic separation studies on the carbon-coated nickel nanoparticles demonstrated that magnetic separation technology offers a simple and efficient method for adsorbent recovery and reuse.

### Full Text

### Preamble

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## Adsorption Performance of Methylene Blue onto Carbon-Encapsulated Magnetic Nickel Nanoparticles

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### Abstract

Carbon-encapsulated nickel nanoparticles (Ni@C NPs) with a core/shell structure were synthesized in-situ by a direct current arc-discharge plasma method through evaporating bulk nickel in a methane atmosphere. Transmission electron microscopy observation revealed a distinct encapsulation structure, with metallic nickel as the core and a graphitic carbon shell 3-5 nm thick. The BET specific surface area was calculated to be  $38.82 \text{ m}^2 \cdot \text{g}^{-1}$  based on  $\text{N}_2$  adsorption isotherms. Surface modification with hydrogen peroxide enabled functionalization with oxygen-containing groups, which improved the wettability and hydrophilicity of the carbon surface. The resulting material could be used as an adsorbent for the dye methylene blue. The effects of adsorption time, initial concentration, and pH value on adsorption capacity were systematically investigated. Adsorption kinetics were studied using pseudo-first-order and pseudo-second-order models, while Langmuir and Freundlich models were employed to fit the adsorption isotherms. Recycling experiments conducted over five adsorption-desorption cycles demonstrated a recovery rate of 69.4% for the collected powder adsorbent. Magnetic separation studies using an external magnetic field confirmed that magnetic separation technology offers a simple and efficient method for adsorbent recovery and reuse.

**Keywords:** composites, carbon-coated nickel nanoparticles, adsorption, methylene blue, magnetic separation

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## Introduction

Organic dyes are indispensable raw materials in industries such as textiles, papermaking, and plastics, and the resulting dye wastewater poses increasingly serious threats to ecological environments and human health [1]. Numerous treatment methods have been developed, including photocatalytic degradation [2], Fenton and photo-Fenton processes [3,4], and chemical precipitation. However, each of these approaches has certain limitations. Adsorption, as an important physicochemical method for treating dye wastewater, offers advantages such as low cost, high efficiency, absence of secondary pollution, and environmental friendliness [5].

Carbon materials, characterized by stable physicochemical properties, large specific surface area, and well-developed pore structure, have been extensively studied for pollutant adsorption. Activated carbon can remove heavy metals, organic dyes, and phenolic pollutants [6-9], but it is expensive, has high costs, and requires harsh desorption conditions. The discovery of novel carbon materials such as carbon nanotubes [10] has sparked new research enthusiasm, particularly in the adsorption field [11,12]. Meanwhile, toxicological studies have shown that carbon nanotubes are toxic to humans and other organisms. Activated carbon particles are small and difficult to separate from solution systems for reuse, and the loss of fine activated carbon particles also damages the ecological environment. Therefore, developing adsorbents with low cost, large adsorption capacity, simple desorption, and recyclability has important practical significance.

Zhang et al. [13] synthesized  $\text{Fe}_3\text{O}_4/\text{C}$  nanoparticles using  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and glucose as iron and carbon sources, respectively, via a hydrothermal method for dye removal from water. Oliveira et al. [14] combined high-adsorption-capacity activated carbon with magnetic iron oxides ( $\gamma\text{-Fe}_2\text{O}_3$ ,  $\text{Fe}_3\text{O}_4$ ) to remove volatile organic compounds. Qu et al. [15] prepared adsorbent materials by incorporating  $\text{Fe}_2\text{O}_3$  particles into carbon nanotubes using a wet chemistry method for treating dye wastewater, followed by simple magnetic separation for adsorbent recovery.

Currently, synthesis methods for magnetic adsorbents involve complex multi-step chemical processes that easily introduce impurities and have limited yield. These impurities can reduce the saturation magnetization of magnetic metal oxides to some extent, affecting magnetic separation efficiency. In this work, we synthesized core/shell structured carbon-encapsulated nickel nanoparticles (Ni@C NPs) in-situ using a direct current arc plasma method. After surface modification with hydrogen peroxide to obtain oxygen-functionalized adsorbents, we systematically investigated the effects of adsorption time, initial dye concentration, and pH value on methylene blue adsorption, and analyzed the adsorption kinetics, thermodynamics, and recycling performance.

## Experimental Methods

### 1.2 Adsorbent Structure Characterization

The nitrogen adsorption-desorption isotherms of Ni@C NPs were measured using a Quanta Autosorb-1 MP automatic gas adsorption analyzer. Zeta potential at different pH values was determined using a Malvern Mastersizer 2000 Zeta potential analyzer. Crystal structure was analyzed with a Panalytical Empyrean X-ray diffractometer (XRD), while morphology, particle size, and distribution were examined using a Tecnai G220S-Twin transmission electron microscope (TEM). Chemical bond vibration types and functional groups were identified using a NEXUS EURO Fourier transform infrared (FT-IR) spectrometer.

### 1.3 Dye Adsorption Experiments

Standard solutions of methylene blue (MB) at concentrations of 0, 5, 10, 15, and 20 mg · L<sup>-1</sup> were prepared, and their absorbance was measured at 665 nm using a 721 visible spectrophotometer to establish a standard calibration curve. For adsorption tests, 50 mL of MB solution at various concentrations was placed in a 100 mL glass conical flask with 50 mg of carbon-encapsulated nickel nanoparticles. The mixture was ultrasonicated in a water bath at (30 ± 1)°C. Samples were taken at predetermined time intervals, filtered through a 0.22 μm membrane, and the filtered solutions were adjusted to 0.1 mol · L<sup>-1</sup> NaOH solutions and 0.5 mol · L<sup>-1</sup> and 1 mol · L<sup>-1</sup> HCl solutions.

The adsorption capacity (q) and removal rate (R, %) were calculated using the following formulas:

$$q_t = \frac{(C_0 - C_t) \cdot V}{m}$$

$$R = \frac{(C_0 - C_t)}{C_0} \times 100\%$$

where C<sub>0</sub>, C<sub>t</sub>, and C (mg · L<sup>-1</sup>) represent the initial concentration, concentration at time t, and equilibrium concentration of MB, respectively; V (mL) is the solution volume; and m (g) is the adsorbent mass. For equilibrium adsorption capacity calculations, t corresponds to the equilibrium time.

### 1.4 Characterization of Adsorption-Desorption Cyclability

For recycling tests, 50 mg of carbon-encapsulated nickel nanoparticles was added to 50 mL of 10 mg · L<sup>-1</sup> MB solution. After ultrasonic adsorption for 20 min at (30 ± 1)°C, the absorbance was measured. The MB-loaded powder was separated using an external magnetic field and desorbed with anhydrous ethanol (repeated three times). This adsorption-magnetic separation-desorption cycle was repeated five times.

## Results and Discussion

### 2.1 Structure, Composition, Specific Surface Area, and Magnetism of Ni@C NPs

The structural, morphological, and compositional analysis results of carbon-encapsulated nickel nanoparticles are shown in Figure 1. Figure 1a clearly reveals the encapsulation structure, with metallic nickel as the core and a layered graphitic carbon coating 3–5 nm thick. Some defects and shared regions are visible on the surface, primarily caused by rapid cooling and solid solution processes. These defect sites also serve as active adsorption sites. Carbon is the key component in the adsorption process, and encapsulating it around the magnetic metal allows full contact with the solution, facilitating adsorption.

The diffraction peaks at (111), (200), and (220) in Figure 1b correspond to metallic nickel, with no nickel carbide or oxide phases detected. Due to the low relative carbon content, its diffraction peaks are not prominent. The average crystallite size of Ni@C was calculated to be approximately 15.5 nm using the Scherrer formula.

A quantity of carbon-encapsulated nickel nanoparticles was compacted into a bulk sample, degassed at 200°C for 3 h to remove physically adsorbed gases, and then tested for N<sub>2</sub> adsorption at 77 K using an automatic gas adsorption analyzer. The specific surface area calculated from the N<sub>2</sub> adsorption isotherm using the BET equation was 38.82 m<sup>2</sup> · g<sup>-1</sup>. The average particle size estimated from this specific surface area was 67.4 nm, significantly larger than the TEM and XRD results. This discrepancy arises from strong agglomeration of particles due to magnetic interactions, which reduces the measured specific surface area.

Magnetization curves of the carbon-encapsulated nickel nanoparticles were measured using a vibrating sample magnetometer (VSM), yielding a saturation magnetization of 34.04 A · m<sup>2</sup> · kg<sup>-1</sup>, which is lower than that of bulk metallic nickel because the surface contains non-magnetic carbon with a carbon content reaching 23% [18]. Nevertheless, this magnetization is sufficient for magnetic separation of Ni@C NPs from aqueous media.

### 2.2 Surface Modification and Dispersibility of Ni@C NPs

Surface modification of carbon-encapsulated nickel nanoparticles did not produce any peaks related to nickel oxides (Figure 1b), confirming that hydrogen peroxide treatment only modifies the surface carbon, which protects the metallic nickel core.

Figure 2 shows the FT-IR spectra of Ni@C NPs before and after modification. The pristine carbon-encapsulated nickel nanoparticles show virtually no peaks except at 3300 cm<sup>-1</sup>, indicating high product purity. After modification, strong O-H stretching vibration absorption peaks appear at 3435 cm<sup>-1</sup> and 3479 cm<sup>-1</sup>. These originate partly from KBr filler absorbing atmospheric moisture during testing and partly from hydroxyl functional groups formed on the carbon surface

through  $\text{H}_2\text{O}_2$  treatment. Peaks at  $2893\text{ cm}^{-1}$  and  $2914\text{ cm}^{-1}$  correspond to symmetric and asymmetric stretching vibrations of methylene C-H groups. The peak at  $1701\text{ cm}^{-1}$  represents carboxyl group vibrations [19], while  $1635\text{ cm}^{-1}$  and  $1067\text{ cm}^{-1}$  correspond to  $\text{-C=O}$  stretching and  $\text{-C-O}$  peaks [20], respectively. Small, scattered peaks between  $2500\text{--}3200\text{ cm}^{-1}$  arise from free O-H bonds of carboxylic acids. These oxygen-containing functional groups are primarily introduced by  $\text{H}_2\text{O}_2$  treatment at defect sites on the surface carbon.

A quantity of carbon-encapsulated nickel nanoparticles was dispersed in deionized water, ultrasonicated for 30 min, and the pH was adjusted with trace amounts of NaOH or HCl solution. Zeta potential measurements for modified and unmodified Ni@C NPs at different pH values are shown in Figure 3. The isoelectric point (pH<sub>iep</sub>), where the potential equals zero, decreases after modification. At the same pH values, the modified nanoparticles show lower zeta potential compared to the unmodified ones, consistent with the introduction of oxygen-containing functional groups during surface modification.

To compare dispersibility, equal masses of carbon-encapsulated nickel nanoparticles before (Sample A) and after modification (Sample B) were dispersed in deionized water and ultrasonicated for 2 min, 5 min, and 10 min, as shown in Figure 4. The modified sample exhibits significantly improved dispersion rates, primarily because the oxygen-containing functional groups formed by hydrogen peroxide treatment alter the wettability of the carbon surface, making the Ni@C NPs more hydrophilic and enhancing their dispersibility.

### 2.3 Adsorption of Methylene Blue by Ni@C NPs

Figure 5 presents the adsorption equilibrium results at different initial MB concentrations. As the MB concentration increases, the removal rate decreases while the adsorption capacity increases. The adsorption capacity is  $9.7\text{ mg} \cdot \text{g}^{-1}$  at an initial concentration of  $10\text{ mg} \cdot \text{L}^{-1}$ , increasing to  $19.7\text{ mg} \cdot \text{g}^{-1}$  at  $30\text{ mg} \cdot \text{L}^{-1}$ . Higher dye concentrations enhance the adsorption driving force, overcoming the resistance for MB molecules to transition from aqueous solution to the adsorbed state, thus increasing adsorption capacity with initial concentration.

Figure 5 also shows that the adsorption process proceeds rapidly during the first 20 min, then slows significantly. The time required to reach adsorption equilibrium increases with initial MB concentration. This occurs because numerous active adsorption sites are available initially, allowing fast adsorption. As adsorption progresses, these sites become occupied, reducing available adsorption points. Additionally, electrostatic repulsion between adsorbed MB molecules hinders further adsorption, decreasing the rate.

The effect of pH on adsorption was investigated by adjusting MB solution pH from 3.2 to 11.5. The adsorption capacity is minimal at pH 3.2 ( $10.7\text{ mg} \cdot \text{g}^{-1}$ ) and increases to  $19.8\text{ mg} \cdot \text{g}^{-1}$  at pH 11.5. MB is a cationic dye that exists primarily as cations ( $\text{MB}^+$ ) in solution. At low pH, excess  $\text{H}^+$  ions compete with  $\text{MB}^+$  for adsorption sites, limiting adsorption capacity. When pH exceeds the

isoelectric point, the Ni@C NPs become surrounded by negative charges, and electrostatic attraction strengthens with increasing pH, facilitating adsorption. Combined with results from Figure 3 and Figure 6, electrostatic adsorption appears to be the primary adsorption mechanism.

## 2.4 Adsorption Kinetics of Dye on Ni@C NPs

Adsorption kinetics investigates the relationship between adsorption rate and activation energy from a kinetic perspective, providing theoretical basis for understanding the temporal distribution of pollutants between adsorbent and aqueous phases. In this work, pseudo-first-order and pseudo-second-order models were used to analyze MB adsorption onto Ni@C NPs.

### (1) Pseudo-first-order model [21]:

$$\ln(q_e - q_t) = \ln q_e - k_1 t$$

where  $q_e$  and  $q_t$  ( $\text{mg} \cdot \text{g}^{-1}$ ) are the equilibrium adsorption capacity and adsorption capacity at time  $t$ , respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the pseudo-first-order adsorption rate constant.

### (2) Pseudo-second-order model [22]:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where  $k_2$  ( $\text{g} \cdot \text{mg}^{-1} \cdot \text{min}^{-1}$ ) is the pseudo-second-order adsorption rate constant.

The fitting results for pseudo-first-order and pseudo-second-order kinetics are shown in Figure 7 and Table 1. As shown in Figure 7, the pseudo-second-order model exhibits better linear relationships, with correlation coefficients all exceeding 0.99. The adsorption capacities calculated from the pseudo-second-order model are essentially consistent with experimental results, further demonstrating that the pseudo-second-order model well describes the adsorption process of MB onto Ni@C NPs. The  $k_2$  value decreases with increasing concentration, indicating that the adsorption rate decreases as concentration increases.

## 2.5 Adsorption Isotherms of Ni@C NPs

Adsorption isotherms study the distribution behavior of adsorbate molecules between liquid and solid phases at adsorption equilibrium. Commonly used models include the Langmuir and Freundlich models.

### Langmuir model linear form [23]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m}$$

A dimensionless separation factor  $R_L$  indicates the feasibility of adsorption:

$$R_L = \frac{1}{1 + K_L C_0}$$

where  $R_L > 1$  indicates difficult adsorption;  $R_L = 1$  indicates moderate adsorption;  $0 < R_L < 1$  indicates favorable adsorption with good performance; and  $R_L = 0$  indicates irreversible adsorption.

#### Freundlich linear isotherm [24]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$$

where  $C_0$  and  $C$  ( $\text{mg} \cdot \text{L}^{-1}$ ) are the maximum initial concentration and equilibrium concentration of dye in solution;  $q$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the equilibrium adsorption capacity;  $q$  ( $\text{mg} \cdot \text{g}^{-1}$ ) is the Langmuir monolayer maximum adsorption capacity;  $K_L$  ( $\text{L} \cdot \text{mg}^{-1}$ ) is the Langmuir model parameter related to adsorption energy;  $K_F$  ( $\text{L} \cdot \text{g}^{-1}$ ) is the Freundlich model parameter representing adsorption capacity; and  $n$  is the heterogeneity factor.

The fitting results using these two models are shown in Figure 8 and Table 2. Based on Figure 8 and the parameters in Table 2, both models fit the experimental results well ( $r^2 > 0.99$ ) under our experimental conditions. The Langmuir parameter  $R_L = 0.019$ , between 0 and 1, indicates favorable adsorption performance. This suggests that MB adsorption onto Ni@C NPs occurs primarily as monolayer adsorption on a homogeneous surface, with interactions dominated by intermolecular forces and electrostatic attraction. The Langmuir model yields a maximum adsorption capacity of  $20.6 \text{ mg} \cdot \text{g}^{-1}$  for MB on Ni@C NPs.

## 2.6 Dye Desorption and Cyclic Reuse

The adsorption-desorption cycling performance of Ni@C NPs is shown in Figure 9. The removal rate remains essentially consistent for the first four cycles, all exceeding 85%, with a slight decrease in the fifth cycle. After five cycles, 34.7 mg of powder was collected, demonstrating a high adsorbent recovery rate of 69.4%. The desorption process is simple, using anhydrous ethanol as a green solvent that does not produce toxic byproducts and can be reused.

## Conclusion

Core/shell structured carbon-encapsulated nickel nanoparticles were prepared in-situ by direct current arc plasma method. Surface modification with hydrogen peroxide yielded oxygen-functionalized adsorbents suitable for methylene blue dye adsorption. Initial pH, adsorption time, and solution pH all affect adsorption capacity. Kinetic analysis showed that experimental results follow the pseudo-second-order model. The adsorption isotherm fits both Langmuir and Freundlich models, with the Langmuir model giving a maximum adsorption capacity of  $20.6 \text{ mg} \cdot \text{g}^{-1}$  for methylene blue. In five cyclic reuse experiments, the removal rate exceeded 85% for the first four cycles, decreasing slightly in the fifth cycle, while the adsorbent recovery rate remained at 69.4%. The desorption process is simple and straightforward.

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