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# Chemically Deposited Boron-Doped Diamond Screen-Printed Electrodes for the Detection of Manganese

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#### ABSTRACT

Manganese ( $Mn^{2+}$ ) is widely used in industrial applications, including steel production, battery manufacturing, and fertilizers. These activities, along with natural processes, contribute to its presence in environmental water. This study investigates the electrochemical behavior of manganese using laboratory-fabricated screen-printed carbon electrodes (SPEs) combining diamond (D), carbon black (CB), and boron-doped diamond (BDD) in eight different configurations: D + BDD, first layer (L1): CB + second layer (L2): D + BDD, CB + D + BDD, or CB pure, each of them with a chlorinated or plain *pseudo*-reference. The screen-printed electrodes were characterized physicochemically and electrochemically, with their electroactive areas and electron transfer resistances calculated to select the best configuration for the electroanalytical application. A voltammetric screening method for Mn<sup>2+</sup> using differential pulse cathodic stripping voltammetry was developed with no preconcentration required with the SPEs L1: CB + L2: D + BDD (chlorinated) and CB + D + BDD (plain). The method exhibited broad linear ranges (1–100 and 10–100  $\mu$ M) and low limits of detections (0.18 and 0.06  $\mu$ M), for each SPE configuration, respectively, making it suitable for detecting Mn<sup>2+</sup> in contaminated environmental water samples. The electrochemical responses showed good stability across all SPEs produced, with a relative standard deviation of less than 10% (N = 3), whether using the same or different electrodes. Interference studies with other metals confirmed the high selectivity of the proposed sensor. Additionally, Mn<sup>2+</sup> was successfully detected in spiked river and lake water samples, achieving recoveries close to 100%. The analytical performance demonstrates strong potential as a simple, rapid, and selective screening method for manganese detection in environmental samples.

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## 1 | Introduction

The detection of manganese within water is vital for both health and environmental reasons. While essential to body function in small amounts, high concentrations of manganese can pose significant health risks. These include neurological effects [1], cognitive and behavioral issues [2], respiratory and cardiovascular problems [3], and liver and kidney damage [4], with vulnerable groups such as infants and the elderly particularly at risk [5, 6]. The presence of manganese can affect the taste of drinking water and lead to discoloration, while within wastewater it can disrupt treatment processes and harm aquatic ecosystems [7]. As such, regular monitoring of manganese levels within water helps to ensure compliance with required health standards, maintaining quality, and safeguards the public and environment.

Several analytical techniques have been reported for the detection of manganese, including atomic absorption spectrometry [8, 9], fluorimetry [10], X-ray fluorescence [11], and inductively coupled plasma atomic emission spectroscopy [12, 13]. These techniques all offer sensitive and selective determination, however, are all laboratory-based and require skilled operators. Consequently, adequate analysis would require methodical sampling, transportation to an appropriate laboratory, and then analysis by a skilled technician. When considering the sheer number of areas that require monitoring to comply with the United Nations Sustainable Development Goal 6-Ensure Availability and Sustainable Management of Water and Sanitation for all [14], this analytical methodology is clearly not fit for purpose. As such, fast and reliable on-site analysis is desired for screening of potential high-risk areas, after which standardized sampling and transportation to laboratories could be performed to validate the results. In this regard, electrochemical techniques offer several advantages, including excellent sensitivity, specificity, and selectivity, cost-effectiveness, rapid and real-time analysis, minimal sample preparation, and portability [15-17].

The electrochemical detection of manganese has been reported using various electroanalytical methodologies [18], including chronoamperometry [7], potentiometry [19], anodic stripping voltammetry [20], cathodic stripping voltammetry [21], and linear sweep voltammetry [22]. These electroanalytical sensing platforms utilize a wide array of working electrodes (WEs), including hanging mercury drop [23], glassy carbon (GC) [24–26], carbon paste (CP), boron-doped diamond (BDD) [27], carbon film (CF) [28], edgeplane pyrolytic graphite (EPPG) [29, 30], gold (Au) [31], platinum (Pt) [21], additively manufactured (AM) [32, 33], and screen-printed (SP) [34, 35]. In particular, screen-printed electrodes (SPEs) offer excellent synergy with on-site electroanalytical monitoring due to their scales of economy, disposable nature, ease of miniaturization, portability, customizability, and high reproducibility [17, 36, 37].

The production of SPEs can be performed by hand or through an automated process, where automation is preferred as it allows for parameters to be optimized and maintained, and highly reproducible electrodes to be produced. SPEs are produced by depositing a combination of layers onto a flat substrate, offering versatility in terms of electrode design, substrate material and flexibility, and ink composition, while also offering excellent scales of economy. In this work, we look to produce SPEs through four different configurations for the WE and two different *pseudo*-reference electrodes (*pseudo*-RE). The WEs studied were boron-doped diamond films grown on differently formed nucleation layers: a layer of diamond nanoparticles (D + BDD); carbon black (CB) as the first layer (L1) and diamond nanoparticles as the second layer (L2) (L1:CB L2:D + BDD); a mixture of CB powder and diamond nanoparticles (CB + D + BDD); and a WE consisting of pure CB (CB pure). The *pseudo*-RE variations included plain and chlorinated silver. We then look to electrochemically characterize these platforms and determine their ability to detect manganese in real environmental waters.

# 2 | Experimental Section

#### 2.1 | Solutions and Samples

Manganese analytical standard (10 g  $L^{-1}$ ) in nitric acid obtained from Sigma-Aldrich (Lancashire, UK) was diluted in water to a concentration of 1.8 mM, and this solution was further diluted in an appropriate supporting electrolyte for electrochemical analysis. Inner-sphere ferro-/ferri-cyanide ( $[Fe (CN)_6]^{4-/3-}$ ) and nearideal outer-sphere hexaammineruthenium (III) ( $[Ru (NH_3)_6]^{3+}$ ) redox probes (1.0 mM in 0.1 M KCl) were used for the electrochemical characterization of the studied electrodes. A Britton-Robinson (BR) buffer solution (0.1 M) was prepared using boric, phosphoric, and acetic acids (purities > 99.9%), with sodium hydroxide (1.0 M) employed to adjust the pH values between 2.0 and 12.0. Acetate and BR buffer solutions (0.2 and 0.1 M) at pH 4.0 were evaluated as supporting electrolytes to study the influence of ionic strength on manganese detection. Sulfuric acid (H<sub>2</sub>SO<sub>4</sub>, 0.1 M) was used for electrochemical cleaning of the WE. All solutions were prepared using deionized water with a resistivity  $\geq 18.2 \text{ M}\Omega \cdot \text{cm}$  from a Milli-Q Integral 3 system (Millipore, UK).

Copper, lead, chromium, cadmium, zinc, and mercury were evaluated as potential interferents in manganese detection using the proposed method and were all of AAS and ICP TraceCERT single element standard (Merck, UK). All other reagents were of analytical grade (purity > 99%). Lead, cadmium, and zinc were purchased from Fluka Analytical (UK), while the remaining reagents were obtained from Sigma–Aldrich (Lancashire, UK). River water samples were obtained in accordance with EPA guidelines from the River Irwell, Greater Manchester, UK (approx. location: 53.517464, -2.302739). Lake water samples were obtained in accordance with EPA guidelines from Drinkwater Park, Greater Manchester, UK (approx. location: 53.519601, -2.298174), filtered through a syringe filter, and spiked with 10 µM and 60 µM manganese for analysis.

# 2.2 | Electrode Production

Carbon-based SPEs were fabricated in the laboratory by the Slovak Diamond Group (Slovak University of Technology in Bratislava, Slovakia) in four different configurations for the WE and two variants for the *pseudo*-RE [3, 38–41]. The WEs studied were boron-doped diamond films grown on differently formed nucleation layers: a layer of diamond nanoparticles (D + BDD); CB as the first layer and diamond nanoparticles as the second layer (L1:CB L2:D + BDD); a mixture of CB powder and diamond nanoparticles

# **SELECTIVE NUCLEATION**



SCHEME 1 | An overview of the selective nucleation (top image) and fabrication of the electrochemical configurations.

(CB + D + BDD); and a WE are consisting of pure CB (CB pure); see Scheme 1. The *pseudo*-RE variations included plain and chlorinated silver. All SPEs featured a three-electrode configuration, comprising a WE, a counter electrode (BDD), and an Ag or Ag/AgCl *pseudo*-RE electrode. The WE had a surface area of  $3.14 \text{ mm}^2$ , with an inner diameter of 2 mm.

This three-electrode system was fabricated using a novel method involving selective nucleation of the working and counter electrodes, while employing screen-printing techniques for the formation of CB WE, different nucleation layers for the BDD growth on WE and CE, REs and the insulating layer; see Scheme 1. A stencil defining the printed design was prepared in a photochemical way using a positive film template and a light-sensitive emulsion FOTECOAT 1019 BLUE (SPT Sales + Marketing, Heidelberg, Germany). The printing was realized using a polyurethane squeegee SERILOR HR1 P0 85 Sh (Fimor, Le Mans, France) and semi-automatic printing machine TY-600H (ATMA, Taoyuan City, Taiwan) with the substrates being fixed with the help of vacuum table. CB pure WE, CB containing nucleation layer (CB + D, L1:CB), and insulating layer were printed using a polyester mesh PME 71-48Y (SEFAR, Heiden, Switzerland) with a mesh count of 71 threads  $cm^{-1}$ . For the printing of D nucleation layers (D, L2:D) and silver electrode a polyester mesh PET 1500 (SEFAR, Heiden, Switzerland) with a mesh count of 120 threads  $cm^{-1}$  was used. For the CB pure WE 20 wt% dispersion of CB (Ensaco 250 G, Imerys Graphite & Carbon) in 10 wt% ethylcellulose (MERCK, viscosity 22 cP 5% in toluene/ethanol 80:20) / diethylene glycol butyl ether (MERCK,  $\geq$ 99%) binder was used. Nucleation layer for D + BDD WE was printed using a dispersion containing 0.4 wt% of diamond nanoparticles (MERCK, <10 nm particle size) in 15 wt% ethyl cellulose/butyl alcohol (CENTRALCHEM, 99.5%) binder. L1:CB L2:D + BDD WE nucleation layer consisted of two separately applied layers, first one printed with 20 wt% dispersion of CB in 10 wt% ethyl cellulose/diethylene glycol butyl ether binder and the second one with 0.4 wt% of diamond nanoparticles in 15 wt% ethyl cellulose/butyl alcohol binder. For the printing of CB + D + BDDWE nucleation layer, the dispersion contained CB (19.6 wt%) and diamond nanoparticles (0.4 wt%) in 10 wt% ethyl cellulose/butyl alcohol binder. Butyl alcohol dispersions were dried at room temperature, dispersions containing diethylene glycol butyl ether at 120°C for 30 min. RE and contact electrodes were printed using AST6025 printing paste (Sun Chemical, Parsippany, NJ, USA) containing silver particles. Layer were subsequently dried at 150°C for 30 min. Chlorinated process to modify the RE involved chronoamperometry with RE connected as WE in constantly stirred 0.1 mol  $L^{-1}$  KCl solution was used for the transformation of Ag to Ag/AgCl. The applied voltage was +700 mV for 30 s. Insulation layer was printed using a printing paste with mineral filler 240-SC Protective Polymer (Vibrantz, Hanau, Germany) with the drying at 150°C for 30 min. All printed layers were dried in a UN 55 laboratory oven (MEMMERT, Schwabach, Germany) with the layers being left before the drying at room temperature for 5 min for the leveling support. The subsequent chemical vapor deposition of 3  $\mu$ m thick BDD films on the substrates nucleated by screen-printing has been described previously [39]. The gas mixture of 1% trimethyl borate and 0.2% CO<sub>2</sub> in H<sub>2</sub> was chosen for its microcrystalline nature and good electrical parameters.

# 2.3 | Instrumental and Apparatus

Electrochemical measurements were performed using a PGSTAT 204 potentiostat (Metrohm Autolab BV, Utrecht, Netherlands) connected to a microcomputer and controlled by Nova 2.1.5 software. Prior to use, SPEs were electrochemically cleaned using cyclic voltammetry (CV) in 0.1 M H<sub>2</sub>SO<sub>4</sub> for 10 cycles over a potential range of -1.0 V to +1.0 V (versus pseudo-reference) at a scan rate of 100 mV s<sup>-1</sup>. The differential pulse cathodic stripping voltammetry (DPCSV) technique was employed to study electrochemical behavior and manganese detection. All analyses were performed using only 30 µL of solution, with measurements conducted in triplicate (n = 3). The DPCSV parameters were optimized for manganese detection through a univariate study, including deposition potential (0.8–1.2 V), time of deposition (0–90s), step potential (2.5–10 mV), amplitude (10–200 mV), modulation time (10–50 ms), and interval time (0.1–0.5 s).

Scanning electron microscopy (SEM) analysis was performed using Thermo Scientific Scios 2 DualBeam microscope (Thermo Fisher Scientific Inc). Raman spectra of BDD films were acquired using a micro-Raman system equipped with a He-Ne laser (632.9 nm, ISA-Jobin Yvon-Dilor-Horiba).

# 3 | Results and Discussion

# 3.1 | SEM and Raman Characterization

This study investigates the electrochemical behavior of manganese using laboratory-fabricated screen-printed carbon electrodes (SPEs) with diamond (D), CB, and boron-doped diamond (BDD) in eight different configurations: D + BDD, first layer (L1): CB + second layer (L2): D + BDD, CB + D + BDD, or CB pure, with a chlorinated or plain reference. This is explored to optimize the conductivity and to minimize background current and of course helping to decrease the detection limits (see later). The electrodes were examined using a scanning electron microscope (SEM) to analyze their surface morphology.

SEM analysis shows polycrystalline BDD films with different surface morphologies as a result of variations in the screen-printing nucleation process (Figure 1). While the use of pure diamond powder resulted in a nearly homogeneous overgrowth of the substrate surface morphology, the addition of CB powder initiated the growth of a cauliflower-like morphology, most pronounced in the L1:CB + L2D + BDD sample (Figure 1b). However, the crystal size range for all BDD samples is approximately the same, indicating similar properties of the layers. SEM images of the CB pure sample show interconnected amorphous carbon particles approximately 30-60 nm in size, forming a layer with a porous morphology (Figure 1d,h). In contrast to the surface morphology, the chemical composition of all three BDD films was not affected by the differences in the nucleation layer, as shown in the Raman spectra (Figure 2). The spectra show the same typical features of highly doped BDD films, in particular the B<sub>1</sub> maximum at approximately 470 cm<sup>-1</sup> and the B<sub>2</sub> maximum at 1200 cm<sup>-1</sup>, both associated with the incorporation of boron, and the zone center phonon mode  $ZCP_D$  maximum of cubic diamond at 1300 cm<sup>-1</sup>, shifted from its original position (1332.9  $\text{cm}^{-1}$ ) due to the Fano effect and phonon confinement [42]. From the position of B<sub>1</sub>, the concentration of Raman sensitive boron can be calculated to be about  $1.35 \times 10^{21}$  cm<sup>-3</sup> [43]. The Raman spectrum of the CB layer contains broad D (1350 cm<sup>-1</sup>), G (1580 cm<sup>-1</sup>), and 2D (2650 cm<sup>-1</sup>) maximum typical of amorphous carbon materials [44]. The maximum at 1470–1400 cm<sup>-1</sup> belongs to the Al<sub>2</sub>O<sub>3</sub> substrate.

# 3.2 | Electrochemical Characterization

All laboratory-produced electrodes in the different configurations -B + BDD, L1: CB + L2: D + BDD, CB + D + BDD, and CB pure, in either chlorinated or plain form—were evaluated for their electrochemical performance. Studies were conducted using the near-ideal outer-sphere redox probe [Ru (NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>



**FIGURE 1** | SEM micrographs of the surface of electrodes (a,e) D + BDD, (b,f) L1:CB + L2:D + BDD, (c,g) CB + D + BDD and, (d,h) CB pure. BDD, boron-doped diamond; CB, carbon black.



**FIGURE 2** | Raman spectra of the electrodes D + BDD, L1:CB + L2: D + BDD, CB + D + BDD, and CB pure. BDD, boron-doped diamond; CB, carbon black.

(1 mM in 0.1 M KCl) and the commonly used inner-sphere probe  $[Fe (CN)_6]^{4-/3-}$  (1 mM in 0.1 M KCl) to understand their performance against molecules with different redox mechanisms. Initially, a scan rate study using CV at  $5-500 \text{ mV s}^{-1}$  was performed to determine the heterogeneous electron transfer rate constant  $(k^0)$  and the electrochemical surface area  $(A_e)$  for each SPE. Figures S1 and S2, Supporting Information present the scan rate studies for electrodes plain and chlorinated silver pseudo-REs, respectively, showing well-defined peaks corresponding to reduction at ~-0.20 V and oxidation at ~-0.10 V for the redox probe  $[Ru (NH_3)_6]^{3+}$ . The insets show the corresponding Randles-Ševčík plots of peak current versus  $\nu^{1/2}$ , with excellent linearity for both oxidation and reduction processes, indicating that the electrochemical processes are in both cases diffusion-controlled. Using the electrochemical data collected from the scan rate studies with [Ru (NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup>, the main electrochemical parameters—peak-topeak separation ( $\Delta E_{\rm p}$ ) at 50 mV s<sup>-1</sup>,  $k^0$ , and  $A_{\rm e}$ —were calculated and are summarized in Table 1 for each SPE configuration. Furthermore, graphs comparing the voltammograms obtained for each electrode configuration using plain and chlorinated silver pseudo-RE are shown in Figure 3A,B, respectively, at a scan rate of  $50 \,\mathrm{mV \ s^{-1}}$ .

It can be observed that all the studied electrodes outperform the CB pure configuration in all parameters. These improvements are attributed to the high surface area and excellent electrical conductivity provided by D and BDD. To further evaluate the electrochemical performance of the laboratory-produced electrodes, a scan rate study  $(5-500 \text{ mV s}^{-1})$  was conducted using the inner-sphere redox probe  $[Fe (CN)_6]^{4-}$  (1 mM in 0.1 M KCl), as shown in Figures S3 and S4, Supporting Information. Clear redox peaks aligned with the probe were observed, and the excellent linearity in the Randles-Ševčík plot inset confirmed the diffusion-controlled nature of the process. Additionally, electrochemical impedance spectroscopy (EIS) was performed with [Fe  $(CN)_{6}^{4-/3-}$  (1 mM in 0.1 M KCl) to determine the solution resistance  $(R_S)$  and charge transfer resistance  $(R_{CT})$  introduced by the SPEs in all configurations. An example of the resulting Nyquist plot is presented in Figure 3C,D. By fitting the data with the appropriate Randles circuit (inset), R<sub>S</sub> and R<sub>CT</sub> were quantified. As summarized in Table 1,  $R_{\rm S}$  decreased from 4738 (±95)  $\Omega$  to

**TABLE 1** | Comparison of the electrochemically active area, heterogeneous electron transfer, and peak-to-peak separations for the SPEs.

			Plain				Chlorina	ted	
Probe	Parameter	D + BDD	L1:CB + L2:D + BDD	CB + D + BDD	CB pure	D+BDD	L1:CB + L2:D + BDD	CB + D + BDD	CB pure
[Ru (NH <sub>3</sub> ) <sub>6</sub> ] <sup>3+</sup>	$A_{\rm e}  [{\rm cm}^2]$	$0.048 \ (\pm 0.001)$	0.049 (±0.002)	$0.047 \ (\pm 0.001)$	$0.034 \ (\pm 0.002)$	$0.049 (\pm 0.001)$	$0.056 (\pm 0.006)$	$0.060 (\pm 0.015)$	$0.034 \ (\pm 0.001)$
	$k_0 \ [{ m cm \ s}^{-1}]$	4.22	3.48	4.22	8.0	4.23	3.53	4.06	8.34
		$(\pm 0.02) \times 10^{-3}$	$(\pm 0.04) \times 10^{-3}$	$(\pm 0.02) \times 10^{-3}$	$(\pm 0.4) \times 10^{-4}$	$(\pm 0.05) \times 10^{-3}$	$(\pm 0.19) \times 10^{-3}$	$(\pm 0.14) \times 10^{-3}$	$(\pm 0.21) \times 10^{-4}$
	$\Delta E_{\mathrm{p}} \; [\mathrm{mV}]$	70 (±2)	80 (±4)	70 (±2)	210 (±9)	70 (±3)	80 (±2)	70 (±5)	210 (±3)
[Fe (CN) <sub>6</sub> ] <sup>4-/3-</sup>	$R_{ m s}$ $[\Omega]$	327 (±7)	671 (±41)	334 (±8)	4852 (±26)	306 (±7)	562 (±36)	311 (±9)	4738 (±95)
	$R_{\rm ct}$ [k $\Omega$ ]	6.5 (±3.4)	5.9 (土0.9)	29.6 (±40.6)	173.5 (±76.5)	$14.6\ (\pm 4.9)$	6.3 (±0.9)	24.3 (±26.9)	136.9 (±58.4)
BDD = boron-doped el	lectrode; CB = car	rbon black; SPE = scr	een-printed carbon electrode,						



**FIGURE 3** | CV voltammograms of 1 mM [Ru (NH<sub>3</sub>)<sub>6</sub>]<sup>3+</sup> in 0.1 mM KCl on SPEs: D + BDD (red line), L1:CB + L2:D + BDD (blue line), CB + D+BDD (magenta line) and CB pure (olive line) at plain (A) and chlorinated (B) configurations, at 50 mV s<sup>-1</sup>. EIS Nyquist plots of [Fe (CN)<sub>6</sub>]<sup>4-/3-</sup> comparing D + BDD (red line), L1:CB + L2:D + BDD (blue line), and CB + D + BDD (magenta line) SPEs at plain (C) and chloridated (D) configurations. BDD, boron-doped diamond; CB, carbon black; EIS, electrochemical impedence spectroscopy; SPEs, screen-printed carbon electrodes.

671 (±41) Ω for electrodes containing D and BDD, which is attributed to the improved conductivity of these materials. Similarly,  $R_{\rm CT}$  decreased from 136.9 (±58.4) kΩ to 29.6 (±40.6) kΩ for the D- and BDD-containing electrodes compared to CB pure, reflecting the enhanced electrical conductivity and increased electrochemical surface area provided by these materials. It is interesting to note that chlorinated of the *pseudo*-reference appeared to impact the electrochemical active area and peak currents, however, not the  $\Delta E_{\rm p}$  and  $k^0$ . This indicates the chlorinated process could be potentially removing binder and increasing the amount of available electroactive material. The complete electrochemical characterization confirms that the incorporation of D and BDD into the WE significantly improves the electrochemical performance of the studied SPEs.

#### 3.3 | Analytical Performance and Application

#### 3.3.1 | Electrochemical Behavior of Manganese

The analytical performance of the electrodes was evaluated by applying them to the detection of manganese (Mn<sup>2+</sup>). The electrochemical behavior of manganese was studied in a 0.1 M BR buffer solution across a pH range of 2.0–12.0, using DPCSV with the L1: CB + L2:D + BDD chlorinated SPE configuration, as shown in Figure 4. This technique involves a preconcentration step in which the electrode potential is maintained at a sufficiently positive value to form insoluble manganese (IV) oxide on the surface of the WE:  $Mn^{2+} + 2H_2O \rightarrow MnO_2 + 4H^+ + 2e^-$ . After a designated preconcentration period, the potential is swept toward the cathodic



**FIGURE 4** | (A) 3D plots of recorded by DPCSV of 1 mM manganese in 0.1 M BR buffer solution with different pH values (from 2.0 to 12.0). (B) Plot of peak potential— $E_p$  (magenta) and peak current— $I_p$  (blue) versus pH for the manganese reduction process at L1:CB + L2:D + BDD chlorinated SPE. BDD, boron-doped diamond; CB, carbon black; BR, Britton-Robinson; DPCSV, differential pulse cathodic stripping voltammetry.

region, generating a characteristic voltammetric stripping peak. This peak results from the electrochemical reduction of manganese (IV) oxide back to manganese (II) [33]. This electrode was selected as the model for initial optimizations due to its excellent performance during the electrochemical characterization step (Section 3.1). The DPCSV technique was employed under the parameters: +0.85 V deposition potential, 60 s time of deposition, -10 mV step potential, 150 mV amplitude, 20 ms modulation time, and 0.1 s interval time, as previously reported by Saterlay et al. [45].

Manganese exhibits a well-documented reduction process in the literature, which is detectable only at pH values below 8.0 on L1: CB + L2:D + BDD chlorinated SPE. This behavior is likely associated with the speciation of manganese [18], as it predominantly exists in the form of  $Mn_xO_x$  in solution at pH  $\ge$  8.0 in this potential window. A pH-dependent behavior was observed, with the peak potential  $(E_p)$  shifting to more negative values as pH increased, as shown in Figure 4B (magenta). A pH of 4.0 was selected for manganese detection using the L1:CB + L2:D + BDD chlorinated SPE due to its good peak resolution and adequate peak current  $(I_p)$ (Figure 4B - 4blue). Subsequently, the acetate buffer at three different concentrations (0.05, 0.1, and 0.2 M) was evaluated at this pH, with 0.2 M acetate buffer proving to be the most effective and chosen for further studies. Subsequently, the parameters of the DPSCV technique were systematically optimized by varying deposition potential (0.8-1.2 V), time of deposition (0-90s), step potential (2.5-10 mV), amplitude (10-200 mV), modulation time (10-50 ms), interval time (0.1-0.5 s), and evaluating the relationship between  $I_p$  and peak width at half height, aiming to achieve selective and sensitive detection of manganese in environmental samples

# 3.3.2 | Manganese (Mn<sup>2+</sup>) Detection

Under optimal conditions (+0.80 V deposition potential, 45 s time of deposition, -10 mV step potential, 200 mV amplitude, 10 ms modulation time and 0.1 s interval time), repeatability, and reproducibility tests were conducted using the same (N=5) and different (N=3) SPEs, where voltammetric peaks obtained for L1:CB + L2:D +BDD chlorinated are shown in Figure 5, while the stability of the electrochemical response for all SPEs is demonstrated in Table S1, Supporting Information.

The proposed method demonstrates consistent measurements across different assays using various SPEs configurations (Figure 5 and Table S1, Supporting Information). The combination of DPCSV and L1:CB + L2:D + BDD chlorinated SPEs exhibited good stability in the electrochemical responses for the manganese reduction process, with low relative standard deviations (RSDs) total for  $E_p$  (<1.0%) and  $I_p$  (<7%). This stability and reliability indicate that the laboratory-produced SPE, combined with DPCSV, is an effective and promising screening method for  $Mn^{2+}$  detection. Subsequently, the working range for manganese determination was evaluated for each of the produced SPE configurations using standard solutions of the analyte ranging from 1 to  $100 \,\mu$ M. The results are presented in Figures S5 and S6, Supporting Information for the plain and chlorinated electrodes, respectively. Pertinent analytical information is provided in Table 2. For the electrode used as a model (L1:CB + L2:D + BDD chlorinated), a detailed representation is provided in Figure 6.



**FIGURE 5** | Plot of  $I_p$  versus number of measurements performed on three different L1:CB + L2:D+BDD chlorinated SPEs. Insets are voltammograms recorded by DPCSV of 1 mM manganese in 0.2 M acetate buffer solution at pH 4.0. Experimental conditions: +0.80 V deposition potential, 45 s time of deposition, -10 mV step potential, 200 mV amplitude, 10 ms modulation time, and 0.1 s interval time. BDD, borondoped diamond; CB, carbon black; DPCSV, differential pulse cathodic stripping voltammetry; SPEs, screen-printed carbon electrodes.

As shown in Figures S5 and S6, Supporting Information and Table 2, all the studied electrodes demonstrated wide linear ranges with low limits of detection (LOD) and quantification (LOQ). Notably, the electrodes containing D and BDD exhibited improved sensitivities compared to those with only CB pure, which recorded lower slopes (indicating reduced sensitivity). These results support the assumption that the presence of D and BDD on the surface of the WE enhances the electroactive area and sensitivity of the SPEs, making them more suitable for analytical applications. Additionally, the electrodes produced by L1:CB + L2:D + BDD displayed wider linear ranges (1–100  $\mu$ M), outperforming the others. It is important to emphasize that the acceptable concentration of Mn<sup>2+</sup> in environmental samples is up to 1.0  $\mu$ M, as stipulated by The European Parliament and of the Council of the European Union (2020) [46].

#### 3.3.3 | Interference Studies and Applications

To assess the real-world applicability of the proposed method in environmental samples, an interference study was conducted in the presence of copper, lead, chromium, cadmium, zinc, and mercury. The results of these interference studies are presented in Figure 7, with a comparison of the electrochemical signal of manganese alone.

As shown in Figure 7, lead, chromium, cadmium, and zinc did not exhibit redox processes under the studied conditions. In contrast, copper and mercury displayed reduction processes at +0.09 V and +0.28 V (versus *pseudo*-RE), respectively. However, these reduction processes have peak potentials sufficiently distant from that of manganese (+0.67 V versus *pseudo*-RE), enabling selective detection in mixtures. Thus, the proposed method demonstrates high selectivity for manganese in complex samples. Next, real river and lake samples were spiked with manganese and analyzed using the proposed method on two electrodes, L1: CB + L2:D + BDD and CB + D + BDD (Figure S7, Supporting

TABLE 2   Electroanalytical performance	e for	Mn <sup>2+</sup>	detection
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		Linear		Slope			
Electrode		range [µM]	Y – intercept [µA]	$[\mu A \ \mu M^{-1}]$	$\mathbf{R}^2$	LOD [µM]	LOQ [µM]
Plain	D + BDD	10-100	2.4 (±0.6)	-0.23 (±0.01)	0.990	0.09	0.32
	L1:CB + L2: D + BDD	1-100	-1.4 (±0.6)	-0.17 (±0.01)	0.985	0.07	0.23
	CB + D + BDD	10-100	-2.9 (±0.9)	-0.37 (±0.01)	0.990	0.06	0.21
	CB pure	20-70	-2.1 (±0.2)	-0.051 (±0.003)	0.983	2.10	6.99
Chlorinated	D+BDD	10-50	$-2.2(\pm 0.5)$	-0.22 (±0.02)	0.984	0.04	0.14
	L1:CB + L2: D + BDD	1-100	-0.33 (±0.03)	-0.155 (±0.006)	0.990	0.18	0.61
	CB + D + BDD	20-100	- 5.3 (±0.7)	-0.12 (±0.01)	0.986	0.20	0.68
	CB Pure	10-70	-0.59 (±0.03)	-0.014 (±0.007)	0.987	0.65	2.16

BDD = boron-doped electrode; CB = carbon black.



**FIGURE 6** | Voltammograms recorded by DPCSV in 0.2 M acetate buffer solution at pH 4.0 on L2:D + BDD chlorinated SPE before (blank: black line) and after (blue lines) addition of 1–100  $\mu$ M Mn<sup>2+</sup>. Experimental conditions were the same as in Figure 5. Inset show linear regression. All measurements were performed in triplicate, and the error bars (black) were smaller than the symbol presented in the inset. BDD, boron-doped diamond; DPCSV, differential pulse cathodic stripping voltammetry; SPE, screen-printed carbon electrodes.

Information). The first electrode was evaluated due to its wide linear range, which encompasses the minimum acceptable  $Mn^{2+}$  concentration, while the second was selected for its high sensitivity (slope  $-0.37 \,\mu A \,\mu M^{-1}$ ). The recovery results are presented in Table 3.

Figure S7, Supporting Information demonstrates that the electrochemical behavior of manganese in environmental water samples is consistent with the standard voltammetric behavior of this substance. Consequently, the proposed method effectively identifies  $Mn^{2+}$  in river and lake water samples, as shown in Table 3, and enables quantification in all matrices studied using two different SPEs. The method demonstrated good recovery values, with recoveries ranging from 87 to 114% and from 93 to 94% for lake and river samples using L1:CB + L2: D + BDD and CB + D + BDD, respectively. These results indicate that the proposed method is not significantly affected by matrix effects, making it reliable for real-world analyses of metal-contaminated



**FIGURE 7** | Voltammograms recorded by DPCSV on L2:D + BDD chlorinated SPE for: cooper (green line), lead (blue lines), chromium VI (orange line), mercury (yellow line), cadmium (violet line), zinc (rose line) and manganese (magenta line). All compounds were at a concentration of 10  $\mu$ M (except mercury at 2  $\mu$ M) in 0.2 M acetate buffer solution (pH 4.0). Experimental conditions were the same as in Figure 5. BDD, boron-doped electrode; DPCSV, differential pulse cathodic stripping voltammetry; SPE, screen-printed carbon electrode.

waters. Table 4 shows a comparison between the main analytical parameters for  $Mn^{2+}$  detection using electroanalytical methods reported to date.

As shown in Table 4, the proposed method exhibits a good linear range, and a low LOD compared to other electroanalytical methods based on SPEs or unmodified electrodes [7, 22, 47, 58]. Additionally, the proposed sensor offers a more environmentally friendly alternative to mercury-based electrodes (e.g., HDME and Hg) [23, 51]. While extremely low LODs have been achieved using techniques such as DP-ASV and AdSV-CSV with Hg electrodes and Formazan-modified GC [51, 53], these methods, despite their higher sensitivity, are more complex and less suitable for on-site screening analyses. A key advantage of the proposed method for  $Mn^{2+}$  detection in water samples is its simplicity, requiring only direct dilution into the supporting electrolyte, which reduces sample preparation steps, requiring a minimum sample volume of  $35 \,\mu$ L for analysis. This

			Recovery $(I_p)$ [%]		
Electrode		$[Mn^{2+}]_{add}$ [µM]	Lake	River	
Chlorinated	L1:CB + L2:D + BDD	30	89.5 (±6.6)	117.0 (±8.8)	
Plain	CB + D + BDD	60	93.6 (±2.9)	94.4 (±7.6)	

CB = carbon black; BDD = boron-doped diamond.

		Linear	LOD		- 1
Electrode	Technique	range [µM]	[µM]	Sample	References
Bare gold	CA	5.0-2000	34.3	Water	[7]
GO-Mn <sub>2</sub> O <sub>3</sub> /SPCE	SWCSV	0.27-18.2	0.121	Tap water	[47]
Graphite	DP-CSV	0.007-1.09	0.055	Mineral waters	[48]
GC-RDE	DP-CSV	-	$6 \times 10^{-3}$	Coastal and estuarine waters	[49]
1- (2-pyridylazo) – 2-naphthol—CPE	DP-CSV	0.01-10.0	$6.9 \times 10^{-3}$	Seawater	[50]
Hg	DP-ASV	-	$1.73 \times 10^{-4}$	Reference materials of seawater, lagaroshiphon major, and cod muscle	[51]
HMDE	DP-ASV	-	0.046	Ground and tap water	[23]
GC	LSV	0.04-1.0	_	River and lake water, raw sugar	[22]
BDD	DP-CSV	0.04-0.173	$8.9 \times 10^{-3}$	Seawater	[52]
Formazan modified GC	AdSV-CSV	$1.8 \times 10^{-3}$ - 0.546	$7.3 \times 10^{-4}$	Spring, tap, mineral, and seawater	[53]
EPPG	DP-CSV	0.025-0.25	$14.2 \times 10^{-3}$	Certified seawater	[30]
ISE	Potentiometric	5.0-100000	-	Multi-vitamin tablet and wastewater	[54]
Mercury film—Ag	DP-ASV	-	$0.3 \times 10^{-3}$	Rainwater	[55]
Gol electrode	ASC	1.5–12 (×10 <sup>-3</sup> )	$1.4 \times 10^{-3}$	Seawater	[56]
CNTs	SW-CSV	0.6-6.7	$93 \times 10^{-3}$	Pond water	[57]
Pd	SW-SCV	0.455-10.9	0.334	Pond water	[58]
Pyrolytic graphite	Potentiometric	0.01-100000	$4.8 \times 10^{-3}$	Wastewater, soil, and vegetables	[19]
Pt	SW-CSV	0.091-0.910	$16.3 \times 10^{-3}$	Pond water	[50]
Additive manufactured electrode	DP-CSV	0.009–2.7	$1.6 \times 10^{-3}$	Drinking water	[33]
GC	DP-CSV	0.05-3.64	0.012	Tap and lake water	[26]
Pt	SW-CSV	0.09-1.82	$10.1\times10^{-3}$	Drinking water	[21]
L1:CB + L2:D + BDD and $CB + D + BDD$	DP-CSV	1–100 and 10–100	0.18 and 0.06	River and Lake water	This work

ITO, indium tin oxide layer; CA, chronoamperometry; SWCSV, square-wave cathodic stripping voltammetry; GO-Mn<sub>2</sub>O<sub>3</sub>/SPCE, graphene oxide and manganese oxide modified screen-printed carbon electrode; GC, glassy carbon; BDD, boron-doped diamond; CPE, carbon paste electrode; EPPG, edge plane pyrolytic graphite electrode; ASC, anodic stripping chronoamperometry; AdSV, adsorptive stripping voltammetry; HMDE, hanging mercury drop electrode; SW, square wave voltammetry; CSV, cathodic stripping voltammetry; DPV, differential pulse voltammetry; CNTS, carbon nanotubes; ISE, ion-selective electrode.

streamlined approach is particularly attractive for on-site screening analyses, minimizing costs and sample usage while maximizing throughput. Furthermore, many methods listed in Table 4 lack linear ranges capable of quantifying  $Mn^{2+}$  concentrations near the regulatory limit (1  $\mu$ M) [46], often necessitating multiple dilution steps. Another notable feature of this

work is the comprehensive evaluation of potential interference from other common metals in water samples. Unlike previous studies, an extensive interference analysis was conducted, demonstrating the high selectivity of the proposed method for  $Mn^{2+}$ detection. Consequently, the method is well-suited for direct translation to field analysis.

## 4 | Conclusions

This study presents a comprehensive comparison of eight laboratory-produced SPEs and the development of a novel electrochemical method utilizing the SPE with enhanced electroanalytical performance for manganese detection in contaminated waters. The findings highlight the increased electroactive area and sensitivity resulting from the incorporation of D and BDD into the SPEs compared to pure CB. The method's electroanalytical performance for detecting Mn<sup>2+</sup> in environmental samples contributes to effective monitoring of metal contamination in water, providing a robust analytical foundation for accurate forensic reporting. This highly sensitive, efficient, and reproducible approach enables the detection and quantification of Mn<sup>2+</sup> in water samples. Using DPCSV, manganese was detected rapidly and sensitively in river and lake samples, achieving LODs below 3.0 µM for all SPEs studied. The laboratory-produced electrodes demonstrated excellent reliability, with stable electrochemical responses across all configurations (RSD <5% for  $E_p$  and <8% for  $I_p$ ). Additionally, the method's minimal sample requirement (35 µL) makes it wellsuited for portable and on-site analyses, simplifying procedures while ensuring accurate results. Thus, this approach offers a promising, rapid, and straightforward alternative for analyzing manganese contamination in aquatic environmental matrices.

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#### **Conflicts of Interest**

The authors declare no conflicts of interest.

#### Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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#### **Supporting Information**

Additional supporting information can be found online in the Supporting Information section.