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N-DOPED POROUS CARBON DERIVED FROM A DEEP EUTECTIC SOLVENT AND ITS APPLICATION IN SOLID-PHASE EXTRACTION OF PROFENOFOS FROM FRUITS

Z DUŠIKOM DOPIRAN POROZNI OGLJIK, PRIDOBLJEN IZ GLOBOKE EVTEKTSKE RAZTOPINE IN NJEGOVA UPORABA ZA EKSTRAKCIJO INSEKTICIDOV IZ SADJA V TRDNI FAZI

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Porous N-doped carbon materials with glucose and urea derived from a deep eutectic solvent, and their performance in determining pesticides were investigated. The carbon materials were characterized with nitrogen absorption, transmission electron microscopy, X-ray photoelectron spectroscopy, and the results showed that they had high specific surface areas, pore volumes and rich functional groups. Under optimized conditions, this method showed a good linearity (0.2–2.0 μg/mL) and high sensitivity (detection limit of 0.023 μg/mL, S/N = 3). The proposed method was successfully applied in an analysis of a fruit sample with recoveries ranging from 97.2 % to 103.3 %, and good reproducibility was achieved. This work revealed great potentials of a porous N-doped carbon material used as an excellent sorbent material in analyzing organophosphorus pesticides.

Keywords: N-doped porous carbon, profenofos, solid-phase extraction

Avtorji v članku opisujejo porozni z dušikom dopirani ogljik izdelan iz glukoze in sečnine, ki sta bili pridobljeni iz globoke evtektske raztopine. Določili so njegove lastnosti za uporabo v analitiki vsebnosti pesticidov. Material na osnovi ogljika so okarakterizirali z dušikovo absorpcijo, presevno elektronsko mikroskopijo in rentgensko fotoelektronsko spektroskopijo. Rezultati karakterizacije so pokazali, da ima le-ta visoko specifično površino preseka,velik volumski delež por in je bogat na funkcionalnih skupinah. Pri optimalnih pogojih je uporabljena metoda pokazala dobro linearnost (0,2-2,0 μg/mL) in visoko občutljivost z mejo detekcije pri 0,023 μg/mL in S/N = 3.Predlagano metodo so avtorji uspešno uporabili za analizo vzorcev sadja z območjem poprave (okrevanja) med 97,2 % in 103,3 % ter dobro ponovljivostjo. V tem članku avtorji v zaključku poudarjajo velik potencial poroznih ogljikovih materialov dopiranih z dušikom in zato predstavljajo odlične absorpcijske materiale za analitične procese določitve pesticidov na osnovi organskih fosfatnih spojin oziroma pesticidov.

Ključne besede: z dušikom dopiran porozni ogljik, organofosfatni insekticidi, ekstrakcija iz trdne faze

1 INTRODUCTION

Organophosphorus pesticides (OPs) have been extensively used around the world over the last decades, and they played an important role in protecting agricultural crops from pests.[1] However, pesticide contamination is present in agricultural products, ground waters, surface waters, lagoons and drinking water. The residues of OPs have become a major concern because of biological effects, long-distance transport and bioaccumulation along the food chain. So, it is of great importance to establish efficient methods for the OP analysis.[2]

Since pesticide residues in food are usually at low or trace levels, sample pretreatment is the key step in an analytical process. The sample preparation method mainly involves liquid-liquid extraction (LLE),[3] solid-phase extraction (SPE)[4–6] and magnetic solid-phase extraction (MSPE)[6–7] where SPE is preferred due to its advantages including the enrichment of analytes, purification of matrix and low organic solvent consumption.

Several materials have been used for the solid-phase extraction of pesticides, like porous carbon,[8] covalent organic framework[9,10] or mesoporous silica material.[11,12] Generally, the surface area and pore structure are the two key factors that affect the performance of an adsorbent. The incorporation of nitrogen into the carbon matrix can provide the basic sites in the form of various N-containing groups such as amine, imine and pyridinic-N. N-doped porous carbon shows excellent characteristics, such as a high surface area, large pore volume and abundant π-electron system, exhibiting great potential as a solid phase extraction adsorbent[13] or a based catalyst.

Recently, a series of porous N-doped carbon materials (CNs) was prepared, having high specific surface areas and pore volumes, derived from a deep eutectic solvent, and these materials showed good performance in the adsorption of organic contaminants from aqueous or oil solutions[14]. In this study, we investigated their performances when used as solid phase extraction adsorbents in a profenofos analysis.

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2 EXPERIMENTAL PART

2.1 Preparation of the porous N-doped carbon materials

All the reagents used in the experiment were analytically pure and used without further purification.

In a typical synthesis,[14] 0.1 mol of glucose was mixed with (0.3, 0.5, 0.6 and 0.7) mol of urea, separately, then these mixtures were heated at 373 K for 2 h while being magnetically stirred. The obtained clear and transparent solutions were heated and microwaved with a power of 900 W for 5 min. Black foam-like products were obtained, and they were carbonized in a nitrogen atmosphere to obtain porous CNs. Individual steps of the carbonization procedure were as follows: (1) heating from room temperature to 623 K at a rate of 2 K/min; (2) maintaining 623 K for 4 h; (3) heating to 1173 K at a rate of 2 K/min; (4) maintaining 1173 K for 10 h. The materials synthesized had mole ratios of glucose and urea of 1:3, 1:5, 1:6 and 1:7, which were denoted as CN-1, CN-2, CN-3 and CN-4.

2.2 Characterization

The CNs were characterized by X-ray diffraction (XRD, Shimazu XRD-6100, Cu K_α radiation λ = 0.154 nm, nickel-filtered). N_2 adsorption/desorption isotherms were measured at 77 K, using a Micromeritics ASAP 2460 analyzer. Specific surface areas were calculated using the BET model. The morphologies of the obtained materials were examined with transmission electron microscopy (TEM, JEM-2010) and scanning electron microscopy (SEM, TESCAN MIRA3). Surface electronic states were studied using X-ray photoelectron spectroscopy (XPS, LAB MK II XPS, a VG ESCA spectrometer with Al K_α radiation; charging effects were corrected by adjusting the C_{1s} peak to 284.6 eV). FT-IR (Tensor II) was employed to characterize the functional groups of the materials.

2.3 Solid-phase extraction process

The solid-phase extraction process for profenofos was as follows: (1) A certain amount of CNs (20–80 mg) was added to the profenofos solution and shaked for 5–25 min; (2) the mixture was centrifugally separated and the supernatant solution was completely discarded; (3) the captured profenofos were eluted from the adsorbent with a 2-mL eluent for 3 times; (4) 10 μL of the resultant desorption solution was injected into a GC-MS system for analysis. The analysis of the desorption solution was carried out on the GC-MS system (SHIMAZU-MS-2010), equipped with a capillary chromatography column.

For the fruit sample analysis, the apples were cut into slices keeping the skin and homogenized, then 5g of NaCl and 20 mL of acetone were added to 10 g of apple pulp. After being shaken for 10 min, the mixture was separated by a centrifuge, and the supernatant solution was injected into GC-MS for analysis.

3 RESULTS AND DISCUSSION

3.1 Characterization

Figure 1 shows XRD patterns of the as-prepared CNs. All the samples exhibited two broad diffraction peaks at about 25°(002) and 44°(101), which can be generally ascribed to the hexagonal graphite and the honeycomb lattice in single-layer graphene,[15,16] respectively, revealing that the catalysts were present in the amorphous structure. The broad signals indicated that the graphitization degree of these materials was very low.

Figure 2 shows N_2 adsorption-desorption isotherms of CN-2 prepared with a glucose/urea ratio of 1:5. According to the IUPAC, the N_2 adsorption-desorption isotherms of CNs should be attributed to a type I isotherm with a typical microporous nature. Table 1 shows some textural parameters, including the specific surface area, pore volume and chemical composition of CN samples It

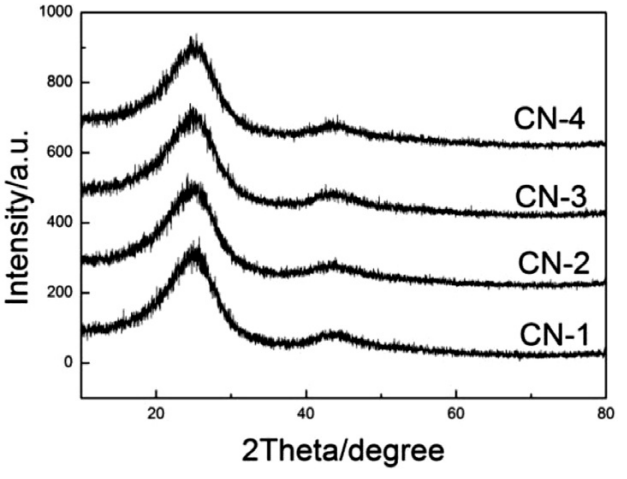


Figure 1: XRD patterns of as-prepared CNs

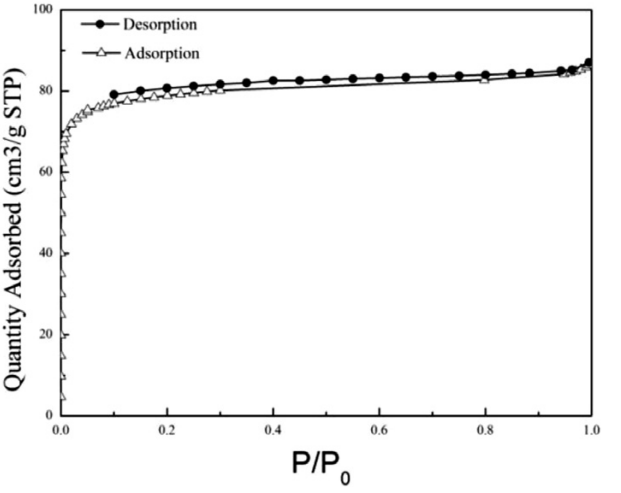


Figure 2: Nitrogen adsorption/desorption isotherm of CN-2

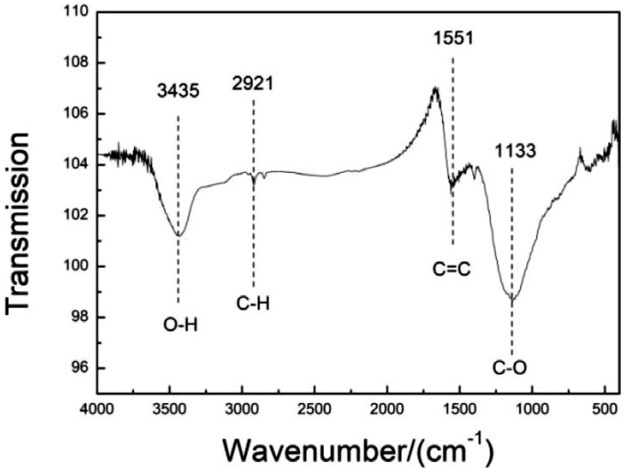


Figure 3: FT-IR spectrum of CN-2

Table 1: Some textural parameters of CNs

sample	S_{BET} (m^2/g)	Pore volume (cm^{-3}/g)	Average pore size (nm)	N (at.%)	C (at.%)	H (at.%)
CN-1	443.692	0.607	2.14	4.6	64.2	1.2
CN-2	568.366	0.618	2.31	5.2	66.2	1.0
CN-3	461.442	0.610	2.17	4.9	62.4	0.8
CN-4	435.331	0.591	2.13	5.0	59.7	1.4

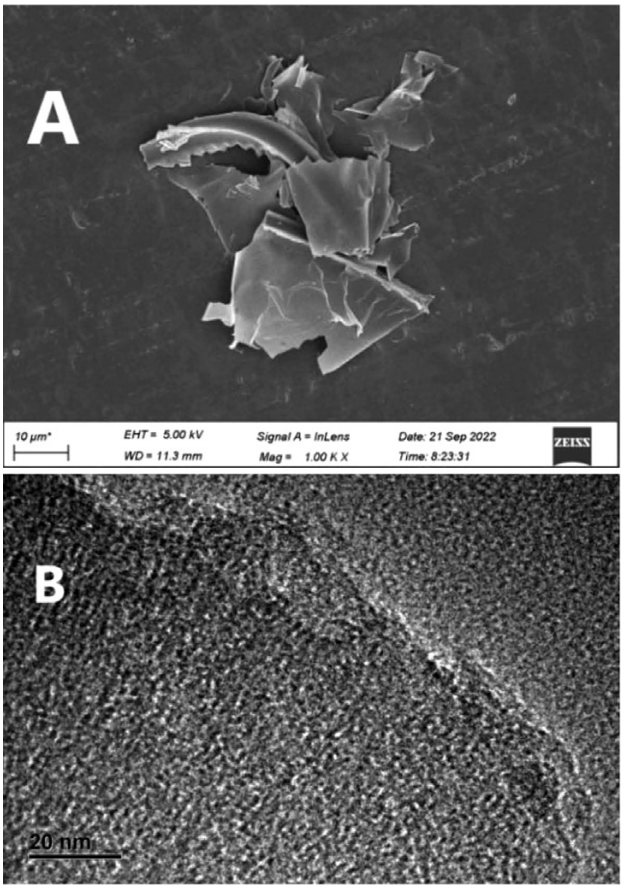


Figure 4: SEM and TEM of CN-2 (A: SEM; B: TEM)

could be concluded that the mole ratio of glucose and urea has an important role in the porous structures of the as-prepared CNs. Among them, CN-2 showed the highest specific surface area of 568 m^2/g, and highest pore volume of 0.618 cm^{-3}/g. Element-analysis data showed that all these materials are mainly composed of carbon, including also a significant amount of nitrogen.

Figure 3 shows the FT-IR spectra of CN-2. The peak centered at 3435 cm^{-1} can be mainly assigned to the stretching vibration of the –OH, $–NH_2$ or =NH groups, while the relative weak peak at 2921 cm^{-1} can be ascribed to the stretching vibration of the –CH group. The stretching vibration of the C-O bond was found at 1133 cm^{-1} and the peak corresponding to the stretching vibration of C=C was located at 1551 cm^{-1}. Identifying the direct spectral evidence of the existence of amide groups and heterocyclic nitrogen was not possible due to the imposition of the absorption band of the C–N and N–H relations of nitrogen compounds on the absorption band of C–C and C–H groups[16–17].

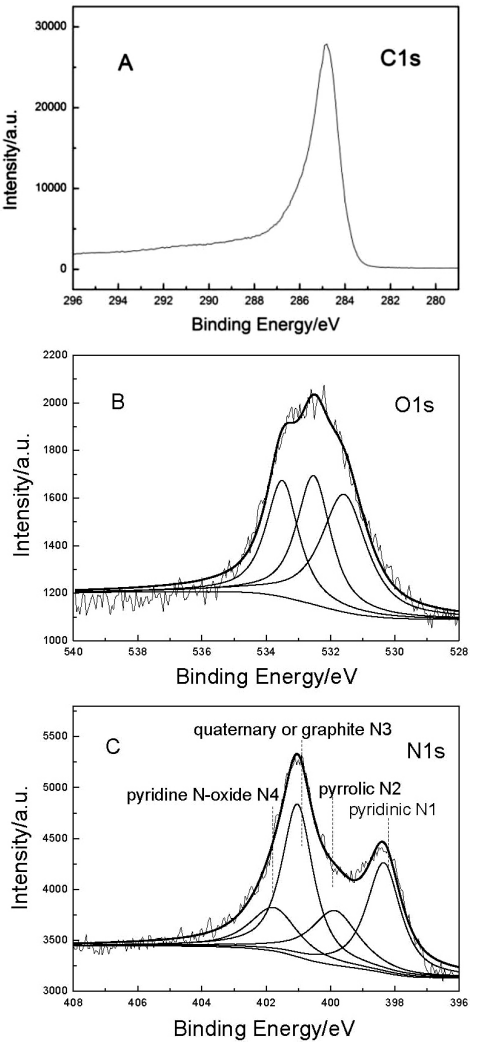


Figure 5: XPS of CN-2 (A: C1s; B: O1s; C: N1s)

Figure 4 shows the morphology and microstructure of CN-2 presented by SEM and TEM. **Figure 4A** shows a SEM image of CN-2; it can be seen that CN-2 shows an irregular film- or layer-like particle structure. **Figure 4B** shows a TEM image of CN-2; a large number of pores is seen and that might be the reason of high S_{BET} and large V_{total}.[14]

Figure 5 shows the XPS of CN-2. **Figures 5A** to **5C** show C1s, O1s and N1s peaks. Generally, the C1s peak can be deconvoluted into three components: Peak 1 (284.7–284.8 eV) is ascribed to pure graphitic or amorphous C–C. Peak 2 (286.1–286.3 eV) is ascribed to the sp2-type carbon such as C-N groups, carbon in phenolic, alcohol or ether. Peak 3 (287.7–288.2 eV) is ascribed to the sp3-type carbon such as C-N bonding states, carbon in carbonyl or quinone groups.[16,17] The O1s peak can be deconvoluted into three components: Peak 1 (530.3–530.7 eV) is ascribed to highly conjugated forms of carbonyl oxygen such as quinone or pyridone groups, Peak 2 (531.7–531.9 eV) corresponds to oxygen in hydroxyl or ethers, while Peak 3 (533.0–533.4 eV) corresponds to oxygen in anhydride, lactone, carboxylic acids, or NO_x. The N1s peak can be deconvoluted into four different peaks: Peak 1 (398.2 eV) is ascribed to pyridinic N, Peak 2 (399.9 eV) is ascribed to pyrrolic N, Peak 3 (400.9 eV) is ascribed to graphite N, and Peak 4 (401.8eV) is ascribed to pyridine N-oxide N.[16,17] Based on the XPS results, the majority of N atoms are associated with the formation of surface as pyrrolic and pyridinic nitrogens, while the other N atoms are incorporated, as a member, into the skeleton of the carbon. It can be concluded that CN-2 shows strong Lewis basicity due to the presence of O- and N-containing groups.

3.2 Performance of absorption

3.2.1 Effect of the sorbent

Figure 6 shows the performances of CNs in the adsorption of profenofos. The results showed that the sorbent had a significant effect on the SPE extraction capacity. CN-1, CN-2, CN-3 and CN-4 exhibited recoveries of 61.5, 71.4, 57.6 and 50.4 %, respectively; CN-2 showed the best performance. This trend was consistent with the S_{BET} of CNs and it was believed that the high S_{BET} of the N-doped carbon was probably due to the adsorption of profenofos.

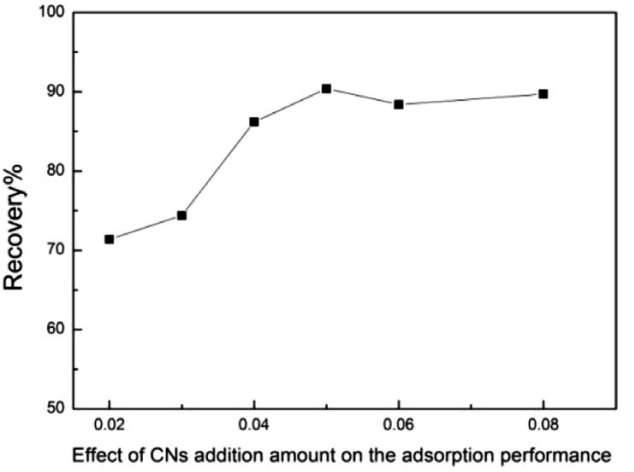


Figure 7: Effect of the CN amount on the adsorption performance
Reaction conditions: sorbent CN-2, extraction time of 10 min, eluent acetone

3.2.2 Effect of the sorbent amount

Figure 7 shows the effect of the sorbent amount in the adsorption of profenofos. It was optimized by varying CN-2 from 0.02 g to 0.08 g. With the increase in the CN-2 dosage, the profenofos increased and reached the maximum value when using 0.05 mg of CN-2. As the sorbent further increased, the extraction showed no obvious change. Thus, in the following experiments, 0.05 g of CN-2 was used to ensure a complete adsorption of profenofos.

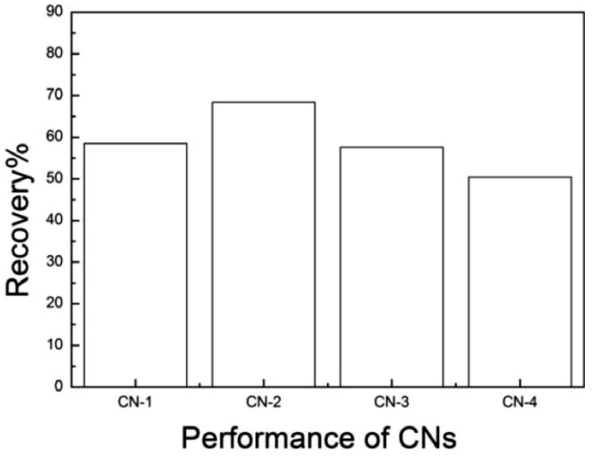


Figure 6: Effect of CNs on the rate of recovering profenofos
Reaction conditions: 0.02 g of the sorbent, extraction time of 10 min, eluent acetone

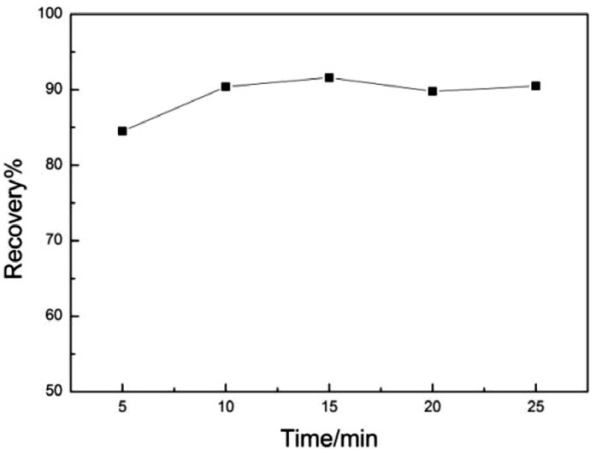


Figure 8: Effect of the extraction time on the adsorption performance
Reaction conditions: sorbent CN-2, sorbent amount of 0.05 g, eluent acetone

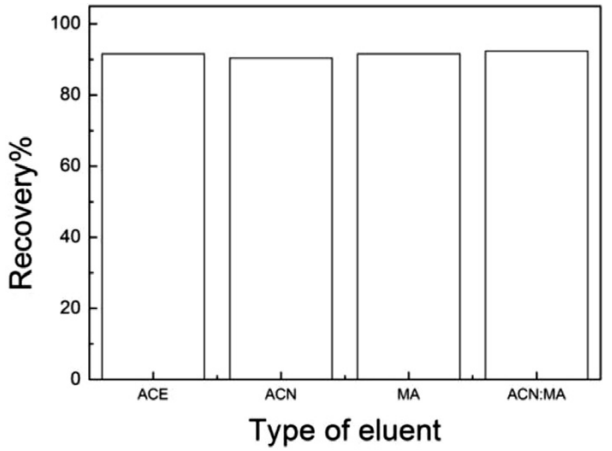


Figure 9: Effect of the eluent type on the adsorption performance
Reaction conditions: sorbent CN-2, sorbent amount of 0.05 g, extraction time of 10 min

3.2.3 Effect of the extraction time

Figure 8 shows the effect of the extraction time on the adsorption performance. As the extraction time is a key factor for SPE, the effect of the extraction time on the recoveries of profenofos was investigated. The effect of the extraction time on the extraction efficiency was studied from the 5th to 25th min. The results showed that the extraction efficiency exhibited no obvious change as the time increased from 10 min to 25 min. Therefore, 10 min was selected for further experiments.

3.2.4 Effect of the eluent type

Figure 9 shows the effect of the eluent type on the adsorption performance. The eluent was crucial for desorption of the target analytes from the adsorbents. In this work, methanol, acetonitrile, acetone and acetonitrile:methanol (3:1) were chosen as the desorption solvents. As shown in **Figure 9**, four types of eluent gave similar desorption yields for all the target analytes under the same extraction and desorption conditions. Hence, acetone was selected as the desorption solvent for further experiments.

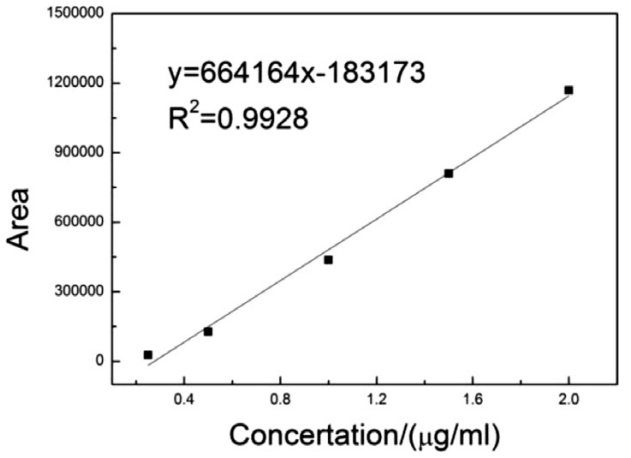


Figure 10: Linearity of CN-2, extraction performance under the optimized SPE conditions
Reaction conditions: sorbent CN-2, sorbent amount of 0.05 g, extraction time of 10 min, eluent acetone

3.2.5 Validation of the method

Figure 10 shows linearity of the CN-2 extraction performance under the optimized SPE conditions. A series of experiments regarding the analytical characteristics including linearity, LOD and RSD was performed to validate the proposed method under the optimized SPE conditions. As shown in **Figure 10**, the proposed method exhibits good linearity in a range of 0.2–2.0 μg/mL with correlation coefficients of ≥0.9928. The LOD (S/N = 3) of the method was 0.023 μg/mL.

Table 2 shows the analysis results for the profenofos in the apple samples. The fruit samples obtained from the local supermarket were analyzed to assess the practical performance of the developed method in a real sample. It can be seen that the spiked recoveries for the apple samples were within 98.2–103.3 %, and the RSDs were in a range of 3.1–7.5 %. All the above results indicate that the method has high sensitivities and satisfactory repeatability.

Table 2: Analysis results for the profenofos in apple samples

sample	added concentration /(μg/mL)	measured /(μg/mL)	recovery /%	relative standard deviation
1	0.4	0.413	103.3	7.5
2	0.5	0.491	98.2	5.3
3	1.0	0.972	97.2	3.4
4	2.0	1.983	99.2	3.1

4 CONCLUSIONS

In this work, porous N-doped carbon materials were prepared with cheap raw materials (glucose, urea) through a deep eutectic solvent. These as-prepared materials with large specific surface areas and pore volumes were successfully applied in the solid-phase extraction of profenofos from fruit, followed by a GS-MS analysis. The results indicated that the as-prepared CNs allowed an excellent adsorption of profenofos and that this developed method with good linearity and high sensitivity can be used also for the analysis of other organophosphorus pesticides in real samples.

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Compliance with ethical standards

The authors have no conflict of interest.

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