Analytical Methods

Determination of organophosphorus in dairy products by graphitic carbon nitride combined molecularly imprinted microspheres with ultra performance liquid chromatography

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1. Introduction

Organophosphorus (OPPs) is a kind of compound used in agriculture to prevent pests and weeds. Because of high control efficiency and short half-life, the OPPs is extensively used (Xie, Zhou, Zhang, Zhao & Zhao, 2021). Unfortunately, excessive use of OPPs cause it to remain in water or soil, and the residues impact non-target organisms negatively through entry into the food chain. OPPs remaining in soil or water is a direct harm to humans. In addition, OPPs can also enter and accumulate in animals and humans through the food chain, indirectly leading to a series of poisonous symptoms (Fu et al., 2022). After entering the body, OPPs can bind to acetylcholinesterase, which can result in a large accumulation of acetylcholine leading to the toxicity and death (Ghorbani et al., 2021).

Code of Federal Regulations has imposed strict restrictions on the residues of OPPs in different types of foods, and the European Union (EU) stipulates that the maximum residue levels (MRL) of OPPs are less than 3 mg/kg in fruits and vegetables (Pang et al., 2020). Furthermore, the restrictions of OPPs on animal derived products are particularly rigorous. This is because the animals such as cows, sheep, and rabbits can obtain OPPs through directly eating plants contaminated by OPPs. Therefore, the dairy products may contain OPPs when dairy cattle are directly exposed to contaminated environment (Fu et al., 2022). Moreover, some countries have stricter residue limits for milk that the MRL for OPPs is in the range of 0.002–0.05 ppm (Fu et al., 2022). Unfortunately, there are still cases where organophosphates are found in dairy products at excessive level. According to a previous report from the EU, 80 of 1183 milk samples contained chlorpyrifos above the MRL. In addition, in a batch of 45 milk samples from Egypt, 20 milk samples contained OPPs above the MRL set by the European Commission (Yuan, Yang, Yu, Xie, Guo & Yao, 2021). Dairy products are a complex matrix, and the OPPs in them are hydrolyzed extremely slow. Therefore, it is difficult to detect the OPPs in dairy products (Lin et al., 2020).

The current methods for detecting OPPs residues usually include gas chromatography (Kaur, Rani, Malik, Kabir & Furton, 2019; Nasiri, Ahmadzadeh & Amiri, 2021), high-performance liquid chromatography (HPLC) (Arias et al., 2020; Zhao et al., 2021), capillary electrophoresis (Chen et al., 2021) and enzyme linked immunosorbent assay (ELISA) (Wu et al., 2021). Among the mentioned methods above, HPLC is widely used and favored by researchers due to its high sensitivity, good selectivity, large-scale application and other advantages. However, dairy products contain complex matrices and some other non-target compounds, which may lead to the false positive results during the test (Gao et al., 2022). Therefore, the development of a novel sample preparation
method is essential for preconcentration and extraction of trace residues of OPPs in dairy products prior to detection.

At present, two commonly used sample extraction and purification methods are liquid–liquid extraction and solid-phase extraction (SPE) (Lin et al., 2020). Among the available methods, the SPE method is favoured by researchers due to its simple operation, good reproducibility, short extraction time, and high concentration capacity (Hashemi & Rezania, 2019). On this basis, some materials such as C18, C8 and PSA were widely used as extraction fillers in the SPE step. (Khan, Arain & Soylak, 2020). As a carbon nitride material, graphitic carbon nitride (g-C3N4) has two-dimensional structure, consisting of triazine ring units linked by an amine group. It possesses unique properties including excellent catalytic activity, chemical stability and easy surface modification (Hashemi & Rezania, 2019). These physicochemical properties make g-C3N4 potential as a novel sample pretreatment material. However, the fillers mentioned above such as C18 and g-C3N4 belong to nonspecific adsorption materials that the competitive adsorption may happen during the sample pretreatment progress, which affects the measurement accuracy. Furthermore, the developed extraction methods based on these fillers cannot be reused. (Wang et al., 2022). So, it is worthwhile to develop a filler with a specific recognition ability to eliminate the interference of impurities in the pretreatment process.

Molecular imprinting technology has been a rapidly developing analytical technique in recent years. It simulates the specific binding of antigens and antibodies in organisms, prepares the polymers that match with a specific target compound in spatial configuration. The prepared polymers are called molecular imprinting polymers (MIP) or molecularly imprinted microsphere (MIM) (He et al., 2021; Liu, Lian, Li, Majid & Wang, 2021). With excellent recognition ability, MIM or MIP can directly adsorb target analytes and minimize background interference. Therefore, MIM or MIP can be applied to the pretreatment and quantitative analysis of trace residues in biological samples with complex matrix.

At present, there have been some reports of combining MIP and g-C3N4 for developing novel analytical methods. Researchers have used MIP, g-C3N4, or other materials in combination for the applications in photochemistry, electrochemistry and detection of some hazardous metal ions (Liu et al., 2020; Pelin Böke, Karaman, Medetalibeyoglu, Karaman, Atar & Lüfti Yola, 2020; Xie, Yang & Li, 2020). In addition, according to some recent reports, g-C3N4 binding to MIP was used for the detection or processing of aflatoxin and tetracycline (Mao et al., 2021; Sun et al., 2019). However, to our best knowledge, there are no reports using MIM/g-C3N4 for the detection of OPPs in dairy products.

In this study, for the combinative utilization of the specific recognition ability of MIM and the adsorption ability of g-C3N4, a composite material (MIM/g-C3N4) was synthesized through the direct polymerization of MIM over the surface of g-C3N4. And then, with the application of MIM/g-C3N4 as filler, a SPE cartridge was prepared for the detection of OPPs in dairy products. The synthesized MIM/g-C3N4 was characterized using some instruments and techniques to determine its structure and the functional group. Some parameters that could affect the SPE performance such as loading solvent, elution solvent, pH and salt concentration were optimized. In addition, the regeneration experiments were also performed to evaluate the stability and reusability of MIM/g-C3N4. Finally, the proposed SPE method was successfully applied with UPLC to selectively recognize and detect OPPs in dairy samples (Fig. 1). This study highlighted the potential of MIM/g-C3N4 for OPPs residue analysis in dairy products.

Materials and methods

2.1. Chemicals and reagents

Coumaphos, chlorpyrifos, diazinon, parathion, ribavirin, amantadine, sulfisomidine and oxytetracycline were obtained from Chemical Metrology & Analytical Science Division, National Institute of Metrology (Beijing, China). Divinylbenzene was supplied from Aladdin Industrial Corporation (Shanghai, China). Ammonium acetate, methacrylic acid, melamine, and 2,2-azobis (isobutyronitrile) (AIBN) and were provided by Tianjin Kemiou Chemical Reagent Co., Ltd (Tianjin, China).

2.2. Synthesis of g-C3N4

The synthesis of g-C3N4 was performed based on the previous study with some modifications (Ma et al., 2015). Briefly, melamine weighted at 12 g was heated to 550 °C in a quartz tube furnace for 4 h. The obtained carbonized product was mixed with HNO3 (65 wt%, 35 mL) for 24 h, and the mixture was then placed in absolute ethanol for 8 h of sonication. Finally, the mixture was centrifuged at 6583 g and the precipitate was corrected. After washed by ultrapure water, the precipitate was dried until the weight was constant, and then the g-C3N4 was obtained.
2.3. Synthesis of MIM/g-C₃N₄

The synthesis of MIM is based on a previous report (Jia, He, Cui, Liu & Wang, 2019). Briefly, 6.4 mL acetonitrile, 0.1 mmol template OPPs, 2.1 mL toluene, 20 mg AIBN and 2 mmol divinylbenzene were put into a flask. After sonication for 5 min, the mixture was stirred and blew under nitrogen for 15 min. Under the sealed condition, the flask was stirred in water bath at 60 °C for 24 h.

The sediments were prepared by centrifugation of the collected suspension (8000 rpm, 30 min). For removing the template molecules, methanol/acetic acid (95:5, v/v) was used to extract the sediments in a Soxhlet apparatus for 72 h, then the methanol/acetic acid was replaced by pure methanol, and the extraction process was continued for 24 h. Finally, the sediments, after washed with methanol, were dried to constant weight at 110 °C for 15 min. The residue was reconstituted by 1 mL methanol and filtered through 0.22 μm for UPLC analysis.

The MIM/g-C₃N₄ was synthesized by directly polymerizing the OPPs in the g-C₃N₄ suspension (Wang et al., 2022). Briefly, 0.3 g of the PPAs, 0.1 g CH₃COONa, and 1.5 mL of acetonitrile were added to 5 mL of a methanol/water (1:9, v/v) mixture. The mixture was stirred at 6583 × g for 10 min, the precipitate was discarded, and the supernatant was taken. The supernatant was evaporated to 5 mL at 40 °C, and diluted with ultrapure water to 10 mL. Equivalent of 10, 100 ng/mL of the OPPs was added to the resulting liquid. The supernatant was dried with nitrogen at 40 °C, and the resulting dried product was dissolved by methanol/water (1:9, v/v) 1 mL, filtered (0.22 μm) and analyzed by UPLC. For milk powder, 10 g milk powder was dissolved in ultrapure water and then fully homogenized at 37 °C, the homogenate was processed as the milk sample (Alahlah, El Maadoudi, Bouchirri, Triqui & Bougtaiba, 2020).

In this study, four OPPs including coumaphos, chlorpyrifos, diazinon and parathion and four other compounds (ribavirin, amantadine, sulfomide and oxytetracycline) were used to determine the absorption capacities of the MIM. In this study, MIMs (coumaphos MIM, chlorpyrifos MIM, 30 mg, respectively) were put into a cartridge (80 μL, 0.5 mL). The cartridge was rinsed with methanol and water at 3 mL, respectively. Then, the vacuum pump was used to filter the standard solution (1 mL/min). The filtrate was washed with methanol and filtered through 0.22 μm for UPLC analysis. In order to evaluate the reusability, the used cartridge was rinsed with methanol and water at 3 mL, respectively.

2.5. Development of MIM/C₃N₄-SPE method

The MIM/C₃N₄-SPE cartridge was prepared as follows: briefly, 30 mg MIM/C₃N₄ was put into an empty cartridge (80 × 5.6 mm, the inner diameter) and washed with methanol (1 mL) and water (1 mL). Then, the vacuum pump was used to filter the standard solution (1 mL/min). The filtrate was used to clean the cartridge, and the remaining analyte was eluted. The filtrate was dried with nitrogen at 40 °C. Then, the residue was reconstituted by 1 mL methanol and filtered through 0.22 μm for UPLC analysis. In order to evaluate the reusability, the used cartridge was rinsed with methanol and water at 3 mL, respectively.

2.6. Sample preparation of dairy products

Milk, yogurt, and milk powder were purchased randomly from local markets, which were analyzed by the developed method. The milk and yogurt samples processing methods were carried out according to the previous reports (Ghorbani et al., 2021; Pan et al., 2022). Briefly, 0.3 g MgSO₄, 0.1 g CH₃COONa and 1.5 mL of acetonitrile were added to 5 mL milk to precipitate protein. After centrifugation of the mixture (6583 g, 10 min), the precipitate was discarded and the supernatant was taken. The supernatant was evaporated to 5 mL at 40 °C, and diluted with ultrapure water to 10 mL. Equivalent of 10, 100 ng/mL of the OPPs was added to the resulting liquid. The supernatant was dried with nitrogen at 40 °C, and the resulting dried product was dissolved by methanol/water (1:9, v/v) 1 mL, filtered (0.22 μm) and analyzed by UPLC. For milk powder, 10 g milk powder was dissolved in ultrapure water and then fully homogenized at 37 °C, the homogenate was processed as the milk sample (Alahlah, El Maadoudi, Bouchirri, Triqui & Bougtaiba, 2020).

2.7. UPLC condition for OPPs analysis

Analytes were chromatographically determined on an ACQUITY H-CLASS UPLC system (Waters Technology, Milford, USA). A HSS C18 column (2.1 × 100 mm, 1.8 μm) maintained at 40 °C was used to separate the four OPPs. The mobile phases were made up of solvent A
The flow rate of the mobile phase was 0.25 mL/min under the gradient elution progress in Table S1. The injection volume was set to 10 μL, and the OPPs were detected at 254 nm and 275 nm.

2.8. Analysis and processing of experimental data

In this study, each measurement was repeated three times, and the data were expressed as mean ± standard deviation (SD). The limits of quantitation (LOQ) and limits of detection (LOD) were determined at signal-to-noise ratios of 10 and 3, respectively. The intraday recoveries were calculated when 6 samples were measured on the same day, and the interday recoveries were calculated when one sample was measured for 6 consecutive days. The coefficient of variation (CV) was calculated with SD/average.

3. Results and discussion

3.1. Characterization of the composite material

The results of Fourier transform infrared spectra were shown in Fig. 2A. It was found that there were distinctive peaks at 3126 cm⁻¹, 1643 cm⁻¹, 1237 cm⁻¹ and 808 cm⁻¹ in the spectrum of g-C₃N₄, which were corresponding to the stretching vibration of N—H bond, C—N bond and out-of-plane bending of triazine. The peak of MIM/g-C₃N₄ contained the peak of MIM (C—H bond 2927 cm⁻¹, C—O bond 1705 cm⁻¹, C—O bond 1448 cm⁻¹) and g-C₃N₄ (triazine ring 808 cm⁻¹). These results indicated that MIM was successfully bound to g-C₃N₄.

The results of scanning electron microscope were showed in Fig. 2B. It was manifest that pure MIM was a sphere with a uniform shape, and the g-C₃N₄ was an irregular flake. Notably, the MIM was evenly distributed over the surface of g-C₃N₄. These results indicated that the synthesis process was feasible and the MIM/g-C₃N₄ were obtained.

Measurement of the N₂ adsorption-desorption isotherms of the MIM/g-C₃N₄ was performed at 77.3 K. MIM/g-C₃N₄ was a specific adsorption material, its ability to identify OPPs was based on imprinted three-dimensional (3D) cavities. Through the calculation of isotherms in Fig. 2C, the Brunauer-Emmett-Telter surface area and Barret-Joyner-Halenda total pore volume were 172.208 m²/g and 0.113 cc/g, which indicated that the MIM/g-C₃N₄ had good adsorption capacity.

Under the environment of flowing air, the thermogravimetric data of MIM/g-C₃N₄ were obtained from 40 to 800 °C (10 °C/min). The results in Fig. 2D showed that the MIM/g-C₃N₄ started to lose weight massively at 300 °C, which suggested that the MIM/g-C₃N₄ began to decompose at 300 °C. In addition, the material had a very slight increase in mass at 250–300 °C. The mass gain is because when the temperature rises, the density of nitrogen becomes smaller, resulting in a smaller buoyancy, and the mass of the sample is higher. In this study, all operations of dairy production analysis were performed at room temperature, so the thermal stability of MIM/g-C₃N₄ could fulfill the request of the subsequent experiments.

3.2. The adsorption capacity of MIM, NIM g-C₃N₄ and MIM/g-C₃N₄

The 3D cavities formed by MIM is determined by the template molecule. Therefore, the choice of template molecule is particularly critical. In this study, three template molecules (coumaphos, chlorpyrifos and diazinon) were selected for the synthesis of MIM, and three kinds of MIM of each template molecule were synthesized by changing the ratio of template molecules to functional monomers, and then their respective adsorption capacities were compared to select the optimal scheme. It could be seen from Fig. 3A that, when the ratio of coumaphos to functional monomers was 1:6, the adsorption capacity was obviously higher than those of the other MIMs. So, the MIM with a 1:6 ratio of coumaphos to functional monomers was selected to synthesize of MIM/ g-C₃N₄.

As shown in Fig. S1, the core structure of the four OPPs was thiophosphate ester, which was almost the same in the 3D conformations of the molecules. Their tetrahedral structures were centered on phosphorus atoms, bond angles between 102° and 115° (Table S2), and the side chains were connected to oxygen atoms in the core structure. Compared with the other 3 OPPs, coumaphos has two 6-membered rings, which have large steric hindrance. The other 3 OPPs could enter the 3D cavities imprinted with coumaphos. Compared with coumaphos, both chlorpyrifos and diazinon have only one six-membered ring, and the steric hindrance is smaller, so the formed 3D cavities are smaller. It is more difficult for other OPPs molecules to enter, so the adsorption capacity of MIM synthesized with chlorpyrifos and diazinon was weaker than coumaphos.

After ensuring the template molecule, the adsorption capacity of the four adsorbents was measured. It could be seen from Fig. 3B that the adsorption capacity of MIM for OPPs was obviously higher than the results of other compounds. The g-C₃N₄ could adsorb eleven compounds, but the adsorption effect was not obvious. This is due to the physical properties of g-C₃N₄ itself, which means that g-C₃N₄ is a non-specific adsorbent. After synthesizing MIM and g-C₃N₄ into a composite material, it was found that MIM/g-C₃N₄ has a high adsorption performance and the ability to specifically recognize the OPPs (Fig. 3B). In
addition, since NIM did not add template molecules during the synthesis process, there were no imprinted cavities on its surface, so it could not adsorb these compounds. What’s more, since the 3D cavity of MIM/g-C_3N_4 did not match the molecular structure of the other four compounds, MIM/g-C_3N_4 could not adsorb the other four compounds. This indicated that the MIM/g-C_3N_4 had good anti-interference ability, and it could specifically recognize the four OPPs.

3.3. Parameter optimization of SPE method

In this study, an SPE method was developed based on MIM/g-C_3N_4 composites, and the parameters affecting the purification effect were optimized.

3.3.1. Loading solvent

Loading solvent provides the appropriate environment for the analyte and affects the recovery. During the experiment, four tested OPPs were diluted with different solvents to 1 μg/mL and loaded onto the MIM/g-C_3N_4 SPE cartridge, and the recoveries were determined, respectively. The results in Fig. 4A showed that, when methanol/water (1:9, v/v) was used as the loading solvent, the recovery of OPPs was the highest. So, it was chosen for the subsequent experiments.
3.3.2. Elution solvent

In this study, four OPPs (1 μg) were diluted with loading solvent and loaded onto MIM/g-C\textsubscript{3}N\textsubscript{4} SPE cartridges. After the adsorption process was completed, the cartridges were eluted with different elution solutions. The results in Fig. 4B showed that methanol/acetic acid (95:5, v/v) had an optimal elution effect, so it was chosen as the elution solvent. During the elution process, acetic acid could break the chemical bond between MIM and OPPs, and the OPPs could easily be eluted, so methanol/acetic acid often performed well as an elution solvent. After that, the volume of elution solvent was optimized. The results in Fig. 4C indicated that 1 mL of elution solvent could elute almost all of the adsorbed OPPs (elution rate > 90 %), so the volume of elution solvent was set at 1 mL for the subsequent experiment.

3.3.3. pH

During the extraction process, the pH of the solution can affect the physicochemical properties of OPPs, thereby affecting the purification effect. In this study, the recoveries under pH from 3.0 to 10 were measured to evaluate the optimal pH. It could be seen from Fig. 4D that the sample recovery rates at the pH of 5.0 and 6.0 were better than other recoveries. In this study, the four selected and tested OPPs all contain phosphorothioate structures, which are easily converted into corresponding phosphoric acid and alcohol in acidic (pH less than 4) and alkaline (pH > 8) solutions (Moinfar, Khodayari, Abdurrahman, Aghaei, Sohrabnezhad & Jamil, 2022). Therefore, the solution pH was adjusted to 6.0 in subsequent experiments.

3.3.4. Salt concentration

According to a previous report, adding salt to the sample may have two opposing effects. On the one hand, adding salt to the sample can lead to analyte precipitation due to the salting-out effect, which helps the MIM/g-C\textsubscript{3}N\textsubscript{4} to adsorb the analyte. On the other hand, the addition of salt causes the solution to become viscous, which is not conducive to the adsorption of OPPs (Gao et al., 2021). During the experiment, the ionic strength was examined by adding 0–10 mM NaCl to the tested samples. The results in Fig. 4E indicated that the ionic strength made no difference on the adsorption effect. Although the addition of salt made the solution viscous, the adsorption capacity was not affected due to the large pore size of the MIM/g-C\textsubscript{3}N\textsubscript{4}. Based on these results, the salt was not used in the SPE process.

In summary, the optimal parameters of the extraction process were: methanol/water (1:9, v/v) was used as loading solvent, methanol/acetic acid (95:5, v/v, 1 mL) was used as elution solvent, solution pH was adjusted to 6, and no salt was added.

3.4. Method performance

In order to evaluate the method performance, four OPPs were diluted with blank milk, yogurt and milk powder extracts, respectively, and determined according to the optimized conditions mentioned above. The results in Table S3 indicated that the LODs of the four OPPs were ranged from 0.2 to 0.8 ng/mL and the LOQs were 0.7–2.6 ng/mL, and the four OPPs had a good linearity from 1 to 10000 ng/mL ($r^2 > 0.999$).

To evaluate the reuse performance of the material, three matrix-matched standard solutions were loaded onto three cartridges, respectively, and then reused 30 times. The results in Fig. 4F showed that MIM/g-C\textsubscript{3}N\textsubscript{4} had a good reusability. After 15 times of use, the OPPs recoveries of the three matrix-matched solutions began to be lower than 90 %. In order to ensure the accuracy of the measurement and the rigor of the experiment, the reusable times were set as 15 times. These results showed that MIM/g-C\textsubscript{3}N\textsubscript{4} was a recyclable and durable absorbent. The reduction in recovery rate might be due to the following two reasons: first, the matrix-matched solution contained impurities, which occupied adsorption cavities and were difficult to elute, so the accumulated impurities reduced the adsorption capacity of the material. Second, the elution solvent could not completely elute the adsorbed analytes, and these accumulated analytes occupied the cavities of the MIM/g-C\textsubscript{3}N\textsubscript{4}, which resulted the reduce of the cartridge absorption.

The chromatograms of the four matrix-matched OPPs solutions were shown in Fig. S2. It can be seen that there were no impurity peaks around the target analyte, this indicated that the cartridge had a good specific purification effect. Then the four tested OPPs were added into the blank milk, yogurt and milk powder samples for analysis, respectively. The results of the dairy products were summarized in Table 1, in which the intraday recoveries were 86.4 to 95.3 % and interday recoveries were 86.1 to 95.4 %. When the matrix effect is between 20 % and 20 %, it indicates the sample preparation method is feasible and has a weak matrix effect. In present study, the results of matrix effect were in

| Samples     | OPNs        | Added (ng/mL) | Intraday recovery | Interday recovery |
|-------------|-------------|---------------|-------------------|-------------------|
| Milk        | Coumaphos   | 10            | 92.8              | 91.1              |
|             |             | 100           | 90.6              | 92.2              |
| Chlorpyrifos|             | 10            | 88.9              | 87.9              |
|             |             | 100           | 93.0              | 95.4              |
| Diazinon    |             | 10            | 86.4              | 86.1              |
|             |             | 100           | 88.6              | 86.3              |
| Parathion   |             | 10            | 90.7              | 90.1              |
|             |             | 100           | 92.5              | 87.7              |
| Yogurt      | Coumaphos   | 10            | 88.1              | 89.9              |
|             |             | 100           | 92.6              | 93.5              |
| Chlorpyrifos|             | 10            | 87.5              | 89.4              |
|             |             | 100           | 93.1              | 90.3              |
| Diazinon    |             | 10            | 89.6              | 92.7              |
|             |             | 100           | 94.6              | 91.1              |
| Parathion   |             | 10            | 87.1              | 89.3              |
|             |             | 100           | 91.3              | 91.6              |
| Milk powder | Coumaphos   | 10            | 95.3              | 94.4              |
|             |             | 100           | 86.6              | 90.8              |
| Chlorpyrifos|             | 10            | 94.5              | 91.1              |
|             |             | 100           | 86.6              | 88.4              |
| Diazinon    |             | 10            | 93.1              | 87.5              |
|             |             | 100           | 94.2              | 93.4              |
| Parathion   |             | 10            | 89.1              | 92.0              |
|             |             | 100           | 89.0              | 95.0              |
simple to synthesize and can be reused many times. Considering the using MIM/g-C3N4, the synthesized MIM/g-C3N4 has a good potential in the purification process of dairy products.

3.5. Real sample detection

In this study, some samples from the local market were analyzed using MIM/g-C3N4 cartridge. From the results, all the samples were negative. Nevertheless, the threat of OPPs to human health cannot be underestimated, especially for the elderly and children.

3.6. Comparison with other methods

With the application of SPE method using MIM/g-C3N4, this study firstly detected the OPPs in dairy products. In order to compare with related studies, the detection methods of OPPs including MIP, HPLC and SPE methods were summarized in Table 2. Compared with the materials reported in other studies, the SPE method based on MIM/g-C3N4 can be reused for 15 times, does not require complicated operation process, and costs less. Due to the physical properties such as strong adsorption and easy modification, g-C3N4 has great potential in sample pretreatment. With the combination of g-C3N4 to MIM, the synthesized MIM/g-C3N4 can be well applied to detect designated compounds with specific recognition ability. Moreover, the composite material of MIM/g-C3N4 is simple to synthesize and can be reused many times. Considering the application in OPPs detection, MIM/g-C3N4 has a good potential in the purification process of dairy products.

4. Conclusion

In present study, a MIM/g-C3N4 composite martial was prepared, and a novel SPE cartridge was developed using the MIM/g-C3N4 for the purification and detection of OPPs in dairy products. The MIM/g-C3N4 has the advantages of specific recognition ability, good extraction effect and reusability. The prepared SPE cartridge was combined with the UPLC method to detect OPP in dairy products, and the results were satisfactory. Therefore, MIM/g-C3N4 may become a potential excellent material in the pretreatment of dairy products for OPPs residue testing.

CRediT authorship contribution statement

Yinchuan Pan: Conceptualization, Formal analysis, Investigation, Methodology, Writing – original draft. Xu Liu: Formal analysis, Investigation, Jing Liu: Data curation, Formal analysis. Jianping Wang: Conceptualization, Project administration, Resources. Juxiang Liu: Supervision, Visualization. Yanxia Gao: Investigation, Methodology, Resources. Ning Ma: Conceptualization, Funding acquisition, Validation, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was financially supported by the Precision Animal Husbandry Discipline Group Construction Project of Hebei Agricultural University (No. 1090064; Baoding, China) and earmarked fund for CARS (No. CARS-36, Beijing, China). The authors have not stated any conflicts of interest.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.fochx.2022.100424.

Table 2

| Material                  | EM          | Analytes | DM     | LOD (ng/g or ng/mL) | Application                                      | Reuse time | Ref.          |
|---------------------------|-------------|----------|--------|---------------------|--------------------------------------------------|------------|---------------|
| Ionic liquid              | CPE         | 5 OPPs   | HPLC   | 2.0–4.3             | coarse cereals                                    | No         | (Zhang et al., 2022) |
| PVA/MGO                   | MSPE        | 5 OPPs   | GC-MS  | 20–80 pg/mL         | juice and water                                   | No         | (Nasiri, Ahmadzadeh & Amir, 2021) |
| MIPSPME                   | QuEChERS    | 11 OPPs  | GC-MS  | 0.74–8.16           | juice                                             | No         | (Wang et al., 2019) |
| Monoclonal antibody       | Coating      | 5 OPPs   | ELISA  | 0.58                | vegetables                                        | No         | (Wu et al., 2021) |
| MIM/g-C3N4                | SPE         | 4 OPPs   | UPLC   | 0.2–0.8             | vegetables, water and barley                      | Yes        | (Huang, Ma, Feng, & Wei, 2019) |

EM: extraction method; DM: detection method; PVA/MGO: magnetic graphene oxide coated with polyvinyl alcohol; CPE: cloud point extraction; MSPE: magnetic solid-phase extraction; SPME: solid-phase microextraction;
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