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Fe₃O₄/hydroxyapatite/graphene quantum dots as a novel nano-sorbent for preconcentration of copper residue in Thai food ingredients: Optimization of ultrasound-assisted magnetic solid phase extraction



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ABSTRACT

Fe₃O₄/hydroxyapatite/graphene quantum dots (Fe₃O₄/HAP/GQDs) nanocomposite was synthesized and used as a novel magnetic adsorbent. This nanocomposite was characterized using scanning electron microscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, X-ray diffraction, energy dispersive X-ray spectroscopy, and magnetization property. The Fe₃O₄/HAP/GQDs was applied to pre-concentrate copper residues in Thai food ingredients (so-called "Tom Yum Kung") prior to determination by inductively coupled plasma-atomic emission spectrometry. Based on ultrasoundassisted extraction optimization, various parameters affecting the magnetic solid-phase extraction, such as solution pH, amount of magnetic nanoparticles, adsorption and desorption time, and type of elution solvent and its concentration were evaluated. Under optimal conditions, the linear range was 0.05-1500 ng mL⁻¹ ($R^2 > 0.999$), limit of detection was 0.58 ng mL⁻¹, and limit of quantification was 1.94 ng mL⁻¹. The precision, expressed as the relative standard deviation of the calibration curve slope (n = 5), for intra-day and inter-day analyses was 0.87% and 4.47%, respectively. The recovery study of Cu for real samples was ranged between 83.5% and 104.8%. This approach gave the enrichment factor of 39.2, which guarantees trace analysis of Cu residues. Therefore, Fe₃O₄/HAP/GQDs can be a potential and suitable candidate for the pre-concentration and separation of Cu from food samples. It can easily be reused after treatment with deionized water.

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1. Introduction

The well known "Tom Yum Kung" is a traditional Thai soup that is generally cooked with giant shrimp (Fig. S1). It is one of the most famous and popular dishes not only in Thailand but also worldwide in Thai restaurants, which have made it well known among foreigners who have experimented with Thai foods. This soup is characterized by its distinct hot and sour flavors with fragrant herbs generously used. To enhance its flavoring appeal, savory complements of various Thai herbs such as chili pepper, tomato, shallot, lemon grass, kaffir lime leaves, galangal, coriander, leek, stinkweed, and lime are combined. The soup is not only delicious but also nutritious. The different herbs and spices used have several health benefits, as they possess antioxidant, antimicrobial, antibacterial antidiabetic, and anticancer properties [1,2].

At a global level, environmental pollution due to heavy metals has become a major concern. Metals are natural occurring chemical compounds. They can be present at various levels in the environment, e.g. soil, water and atmosphere. Metals can also occur as residues in food because of their presence in the environment, as a result of human activities such as farming, industry or car exhausts or from contamination during food processing and storage. People can be exposed to these metals from the environment or by ingesting contaminated food or water. Their accumulation in the body can lead to harmful effects over time, depending on the dose and toxicity. Among the heavy metals, copper is an essential micronutrient that is indispensable for life as it is involved in various biological processes [3]. It plays a central role in human

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