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Ultrasonic-assisted recycling of Nile tilapia fish scale biowaste into low-cost nano-hydroxyapatite: Ultrasonic-assisted adsorption for Hg^{2+} removal from aqueous solution followed by "turn-off" fluorescent sensor based on Hg^{2+}-graphene quantum dots

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ABSTRACT

This study was planned to recycle calcium and the phosphorus-rich Nile tilapia fish scale biowaste into nano-hydroxyapatite (FHAP), using ultrasonic-assisted extraction of calcium and phosphorus from fish scales, which was optimized in term of extraction time, acid concentration, extraction temperature, and ultrasonic power. These two elements were determined simultaneously by inductively coupled plasma atomic emission spectrometry and the FHAP phase was formed upon addition of the extracted element solution in alkaline medium using homogenous precipitation assisted with ultrasound energy. The FHAP adsorbent was characterized by x-ray diffraction, scanning electron microscopy, energy dispersive spectroscopy, transmission electron microscopy, Fourier transform infrared spectroscopy, and Brunauer-Emmett-Teller. A combination of FHAP and the ultrasonic method was then used to remove Hg^{2+} from aqueous solution. Four significant variables affecting Hg^{2+} removal, namely, adsorbent dosage, pH, ultrasonic power, and adsorption time, were studied. The results exhibited that the optimal conditions for maximizing the removal of Hg^{2+} were 0.02 g adsorbent dosage, pH 8, 0.4 kW ultrasonic power, 20 min adsorption time, and 30 °C adsorption temperature. The sorption mechanism of Hg^{2+} was revealed by isotherm modeling, indicating that FHAP adsorbent has a potential for Hg^{2+} removal in aqueous media with the maximum adsorption capacity being 227.27 mg g^{-1}. This adsorption behavior is in agreement with the Langmuir model as reflected by a satisfactory R^2 value of 0.9967, when the kinetics data were fitted with pseudo-second-order. Therefore, the FHAP could be an alternative adsorbent for the ultrasonic-assisted removal of Hg^{2+} at very high efficiency and within a very short period of time.

1. Introduction

Nanotechnology has applications in all divisions of science and technology with diverse substances being prepared and used for the elimination of water pollutants and numerous attempts being made to discuss various aspects of water treatment by adsorption using nano-adsorbent materials [1]. The nanomaterial-based sorbent is an excellent solid phase due to its demonstrated ability to elevate, to a great extent, the sorption capacities of the target analytes. This is because of a special feature of nano-scaled materials, i.e., high surface-area-to-volume ratio, making it a promising solid sorbent for adsorption procedures and homogeneous distribution in solution. Fish is consumed worldwide on a day-to-day basis contributing toward a huge amount of fish biowaste, comprising of fish scales. This may leave residues in the environment leading to health problems and pollution if not properly treated or utilized. Fish scales have a potential for reuse as raw material or could be converted into valuable products, which could be an effective measure toward waste management of fish biowaste, resulting in a lower environmental impact. Over the past several years, fish scales which are rich in calcium and phosphorus, have been used for the synthesis of calcium hydroxide phosphate (IUPAC name) or hydroxyapatite (HAP, $Ca_{10} (OH)_2 (PO_4)_6$) by several methods. HAP has been extensively studied due to its practical applications and natural occurrence and is used as an artificial bone substitute in orthopedic, neuro, dental, and plastic surgeries [2]. In addition, HAP and its composite can also be utilized as an alternative adsorbent [3,4]. HAP is prepared by precipitation methods using calcium nitrate ($Ca (NO_3)_2$, potassium dihydrogen phosphate (KH_2PO_4), and ammonia (NH_3) [5] or by using phosphoric acid (H_3PO_4) solution with calcium hydroxide ($Ca(OH)_2$) [6]. The development of alternative methods toward eco-friendly experimentation has greatly progressed. For example, the preparation of HAP from *Labeo rohita* fish scales was performed by Modal et al. [7].

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