DEVELOPMENT OF BIOSORBENT FILM BASED ON EGGSHELL AND ORANGE PEEL FOR REMOVAL OF HEAVY METAL IONS

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FACULTY OF FOOD SCIENCE AND NUTRITION
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DECLARATION

I hereby declare that the material in this thesis is my own except for quotations, equations, summaries, and references, which have been duly acknowledged and clearly cited its sources.

21 Jun 2023

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ABSTRACT

In Malaysia, contamination of food with heavy metals such as cadmium (Cd), lead (Pb), arsenic (As), chromium (Cr), and copper (Cu) is common. Besides, the production of large amounts of food biowaste contributes to environmental pollution. The food biowaste materials can be used to produce biosorbents, thereby biosorption becoming a more attractive method for removal of heavy metal ions. Herein, a film based on eggshell-orange peel powder-banana starch was developed for removal of heavy metal ions in foods. Optimizing the materials concentration was achieved through response surface methodology (RSM) using central composite design (CCD) which is the best alternatives to improve the production process of biosorbent film. The physical properties of films include thickness, density, porosity, colour, water solubility, moisture content, water absorption, and water vapor permeability were characterised. The morphology properties of a film have been analysed using field-emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDX), atomic force microscopy (AFM) and x-ray diffraction (XRD) analysis. The chemical properties of the film were determined using Fourier-transform infrared (FT-IR) spectroscopy. The removal efficiency of the metal ions onto film at different contact time, pH, adsorbent dosages, and different metal ion concentrations were analysed by using atomic absorption spectroscopy (AAS) where increasing of each of the factors would increases the metal ions removal. The effect of removing heavy metal ions in fish, cereal, and red brown rice samples extract were investigated using inductively coupled plasma mass spectrometry (ICP-MS). The incorporation of eggshell and orange peel has increased the thickness, density, and porosity, and decreased the water solubility, absorption and water vapor permeability of films. Film morphology was shown the rough surface and transparent which contains of various functional groups such as alkane (C-H), hydroxyl (O-H), carbonyl (C=O), carbonate (CO_3^{2-}), and carboxylic acid (-COOH) groups that has ability as biosorption materials. The film exhibited highest removal rates for Cd (99.69%), Pb (72.05%), Cu (68.51%), Ni (31.11%) and Cr (19.78%) ions. The study presented here

suggests that these films could serve as both biosorbents and packaging materials in the food industry. Food quality can also be significantly improved by using such technologies.

ABSTRAK

PEMBANGUNAN FILEM BIOPENJERAP BERASASKAN KULIT TELUR DAN KULIT LIMAU UNTUK PENYINGKIRAN ION LOGAM BERAT

Di Malaysia, pencemaran makanan dengan logam berat seperti kadmium (Cd), plumbum (Pb), arsenik (As), kromium (Cr), dan kuprum (Cu) adalah perkara biasa. Selain itu, pengeluaran sejumlah besar sisa makanan menyumbang kepada pencemaran alam sekitar. Bahan sisa makanan boleh digunakan untuk menghasilkan biopenjerap, dengan itu biopenjerapan menjadi kaedah yang lebih menarik untuk penyingkiran ion logam berat. Di sini, filem campuran berasaskan serbuk kulit telur-kulit oren-kanji pisang telah dibangunkan untuk penyingkiran ion logam berat dalam produk makanan. Kepekatan optimum telah dicapai melalui kaedah gerak balas permukaan (RSM) menggunakan pusat reka bentuk komposit (CCD) yang merupakan alternatif terbaik untuk meningkatkan proses pengeluaran filem biopenjerap. Sifat fizikal filem termasuk ketebalan, ketumpatan, keliangan, warna, keterlarutan air, kandungan lembapan, penyerapan air, dan kebolehtelapan wap air telah dicirikan. Sifat morfologi filem telah dianalisis menggunakan mikroskop elektron pengimbas pelepasan medan (FESEM), spektroskopi sinar-X penyebaran tenaga (EDX), mikroskop daya atom (AFM) dan analisis pembelauan sinar-X (XRD). Sifat kimia filem ditentukan menggunakan spektroskopi inframerah fourier transformasi (FT-IR). Kecekapan penyingkiran ion logam pada filem pada masa sentuhan, pH, dos penjerap dan kepekatan ion logam yang berbeza telah dianalisis dengan menggunakan spektrometer serapan atom (AAS) di mana peningkatan setiap faktor akan meningkatkan penyingkiran ion logam. Kesan penyingkiran ion logam berat dalam ekstrak sampel ikan, bijirin, dan beras perang merah telah disiasat menggunakan spektrometri jisim plasma gandingan induktif (ICP-MS). Penggabungan kulit telur dan kulit oren telah meningkatkan ketebalan, ketumpatan, dan keliangan, dan mengurangkan keterlarutan air, penyerapan dan kebolehtelapan wap air filem. Morfologi filem menunjukkan permukaan kasar dan lutsinar yang mengandungi pelbagai kumpulan berfungsi seperti alkana (C-H), hidroksil (O-H), karbonil (C=O), karbonat (CO_3^{2-}), dan kumpulan asid karboksilik (-COOH). yang mempunyai keupayaan sebagai bahan *biopenjerapan. Filem ini mempamerkan kadar penyingkiran tertinggi untuk ion Cd (99.69%), Pb (72.05%), Cu (68.51%), Ni (31.11%) dan Cr (19.78%). Kajian yang dibentangkan di sini menunjukkan bahawa filem ini boleh berfungsi sebagai biopenjerap dan bahan pembungkusan dalam industri makanan. Kualiti makanan juga boleh dipertingkatkan dengan ketara dengan menggunakan teknologi tersebut.*

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LIST OF ABBREVIATIONS

AAS	-	Atomic absorption spectroscopy
AFM	-	Atomic force microscope
ATSDR	-	Agency for toxic substances and disease registry
BS	-	Banana starch
CCD	-	Central composite design
EDX	-	Energy dispersive x-ray
ESP	-	Eggshell powder
FAO	-	Food and agriculture organization
FDA	-	Food and drug administration
FESEM	-	Field emission scanning electron microscopy
FTIR	-	Fourier transform infrared
ICPMS	-	Inductively coupled plasma mass spectrometry
MC	-	Moisture content
OPP	-	Orange peel powder
RSM	-	Response surface methodology
SEM	-	Scanning electron microscopy
TEM	-	Transmission electron microscopy
WA	-	Water adsorption
WHO	-	World health organization
WS	-	Water solubility
WVP	-	Water vapour permeability
WVTR	-	Water vapor transmission rate
XRD	-	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 Research background

In an era of increasing population, food, transportation, housing, medicines, and technology are in high demand. In order to meet these demands, raw materials must be extracted directly from the environment, thus leading to an increase in improperly discarded waste (Morita et al., 2021). These residues can have serious environmental consequences if they are not disposed of properly. On a global scale, agricultural production has significantly damaged the environment, depleting soil, air, and water resources, and endangering human health. A total of 998 million tons of agricultural waste are expected to be produced each year. Global population is predicted to reach nearly 10 billion by 2050, but an agriculture path to sustainment has not yet been identified (Duque-Acevedo et al., 2020). A variety of agricultural wastes are used for removing heavy metals, including rice husks, chicken eggshells, palm fruit shells, fruit seeds, nutshells, and fruit peels. Households and other food processing industries dispose of these agricultural wastes everywhere (Kumar et al., 2017).

Meanwhile, metal contaminants in food can occur at various stages of production, including growth, in-plant processing, post-harvest handling, preparation for consumption at home and cooking (Aytekin et al., 2019). The chemical and biological degradation of heavy metals makes them particularly hazardous. Generally, they remain in the environment for hundreds of years once released, usually as a result of industrial or mining activities. As a result, they accumulate in organic tissues and plants. Despite being highly toxic and non-biodegradable, heavy metals remain in the environment, enter the food chain through crops, and eventually cause various diseases and accumulate (Yan et al., 2020). Consequently, heavy metal ions must be removed from food as part of food monitoring.

Various techniques for removal of heavy metal ions, including ion exchange, membrane separation, electrochemical or chemical precipitation, reverse osmosis, solvent extraction, adsorption and electrodialysis (Peigneux et al., 2020; Shrestha et al., 2021). Among these, the biosorption process has the advantage of low cost, availability, high efficiency, ease of operation, environmental friendliness and insensitivity to toxic substances (Burakov et al., 2018). Metal ion biosorption is greatly influenced by the functional groups in biosorbents. Most biosorbent materials industry uses activated carbon (Ramos et al., 2022b). However, production and material recovery losses make the treatment process more expensive (Ramos et al., 2022a). Consequently, it is necessary to find low-cost biosorbents for eliminating metallic ions from food. Numerous studies have been conducted with different biosorbents derived from agro-waste in recent years, such as orange peel (Pavithra et al., 2021), passion fruit peel (Ramos et al., 2022a), rice husk (Priya et al., 2022b), watermelon peel (El-Nemr et al., 2022), banana peel (Dhevagi et al., 2019) and eggshell (Ehsanpour, Samani & Toghraie, 2023).

Chicken eggshell is still undervalued as a waste product that can damage the environment and public health when improperly discarded since it may promote the growth of microorganisms, including pathogenic microorganisms, and attract disease vectors and predators (Ayodele et al., 2021). Malaysia produces approximately 642,600 tons of chicken eggs per year and is expected to generate 70,686 tons of eggshell waste per year (Sethupathi et al., 2017) because eggs are a common ingredient in various products, including cakes, fast food, and everyday meals. As a result of higher production costs in 2022, egg production was reduced from 160,000 eggs per day to 120,000 eggs per day. This was due to the ringgit opening at 4.7 against the dollar that year (TheStar, 2022). However, there is still an abundance of chicken eggshells in landfills as Malaysians consume eggs daily. Biosorbents derived from chicken eggshells are emphasised by several authors for its potential economic value (Chen et al., 2021; Lee et al., 2022), have a high amount of calcium carbonate ($CaCO_3$), which makes them an ideal adsorbent material for the treatment of soils and water contaminated by metallic ions (Lee et al., 2022). In addition, the porous nature of eggshells makes the residue a potential adsorbent to remove various pollutants present in aqueous solutions (Tamang & Paul, 2022).

Orange peels are routinely discarded into the environment, and the number continues to rise in tandem with population growth, posing a problem (Akinhanmi et al., 2020). Due to its essential ingredients, hemicellulose, cellulose, lignin, and pectin, which contain functional groups as probable metal-binding sites, researchers have recently employed orange peel as a biosorbent to remove various heavy metals and hazardous oxyanions (Mora et al., 2020; Abd-Talib et al., 2020). Pavithra et al. (2021) previously observed that the adsorption capacity of chitosan-based orange peel hydrogel composites was 80.43% for chromium ions and 82.47% for copper ions. Apart from this, Akinhanmi et al. (2020) found that the adsorbent from orange peel has a removal efficiency of 128.23 mg/g as determined by the Langmuir isotherm. Moreover, Guiza (2017) discovered that the maximum uptake of copper ions in raw orange peels was 63 mg/g.

In the present study, eggshells and orange peels are evaluated as effective biosorbents for removing heavy metal ions from food. This research designed the biosorbent film based on eggshell and orange peel using a simple casting method, forming a porous structure with large functional groups distributed within it, achieving highly effective adsorption of heavy metal ions. As a result of its unique film-shaped structure, the biosorbent was easy to collect, and its three-dimensional structure allowed water to move freely throughout it, thus enabling rapid regeneration. However, it is imperative to conduct thorough investigations to determine their effectiveness in removing heavy metals despite the possibilities associated with the incorporation of eggshell powder and orange peel powder with banana starch. In previous studies, eggshell and orange peel were evaluated separately for their effects on wastewater treatment. There has been limited research on the impact of all of these constituents together on foods in a unified film formulation. The primary goal research focuses on optimisation of biosorbent film based on eggshell and orange peel, characterising the physicochemical properties of the biosorbent film based on eggshell and orange peel, and investigating the biosorption efficiency of the biosorbent film based on eggshell and orange peel in removing heavy metal ions.

1.2 Problem statement

Food waste represents vast amounts of wasted agricultural inputs which contribute to environmental problems such as water pollution, greenhouse gas emissions, loss of biodiversity, and soil erosion (Conrad, 2020). According to Solid Waste and Public Cleansing Management Corporation (SWCorp) Malaysia, the household sector accounts for 45% of the 17,000 tons of food waste generated daily in Malaysia. About 4,080 tonnes of food waste is classified as still edible, with enough to feed 3,000,000 people three meals a day (Zainal, 2021). For example, the production volume of fresh oranges in 2019-2020 was about 46.06 million tonnes, contributing to an increase in orange peel waste disposed of into the environment and causing further pollution (Akinhanmi *et al*., 2020). Besides, chicken eggshells are waste material from hatcheries, households, and the fast-food industry that is abundant and readily available worldwide. Without proper management, their disposal contributes to environmental pollution (Kiew *et al*., 2016).

Heavy metals in food are a current problem contaminating the food chain and harming human health. Contamination of food with heavy metals can come from a variety of sources. Pollution of the soil from which the food is produced, sludge residues, chemical fertilisers and pesticides used in agriculture, and other materials are the most serious. Since heavy metal pollution comes from so many different sources, a wide range of foods are contaminated with heavy metals, including plant-based goods such as grains, wheat, rice, mushrooms, and edible roots, as well as animal-based foods such as fish, molluscs, and crustaceans. Fish are particularly vulnerable to heavy metal contamination because heavy metals are bio-accumulative in the food chain. When heavy metals accumulate in aquatic environments, fish ingest them through their food and accumulate them during their lifetime (Masindi & Muedi, 2018). Malaysians are the biggest consumers of seafood, either fresh or processed. Pollution has challenged the safety of seafood, including heavy metals (Jeevanaraj et al., 2020). Since cereal crops are also essential to human nutrition, heavy metals can adversely impact our health through their health hazards or their influence on wholesome nutrition. Agricultural runoff and pesticides containing heavy metals are responsible for the elevated concentrations in cereals (Adam, Sackey & Ofori, 2022). Furthermore, brown rice has a tendency to accumulate toxic metals such as arsenic, cadmium, lead, and long-term exposure to heavy metals through brown rice consumption can be both non-cancerous and carcinogenic (Fan et al., 2017; Zakaria et al., 2021). Thus, excessive exposure to these heavy metals can leave humans with carcinogenic effects and contribute to severe and ultimately fatal heart attacks (Younis et al., 2021).

1.3 Significance of research

The significance of this research was the utilisation of food waste for the production of valuable materials such as eggshells and orange peels, which serve as absorbents for the removal of heavy metals. As food production increased, it also increased the amount of waste generated from it. These cheap, readily available, and large amounts of waste can be used as bio adsorbents in their natural or modified form for removing heavy metals from food samples and wastewater. Using food waste for heavy metal removal can solve environmental and heavy metal pollution problems (Ahmad & Zaidi, 2020). Furthermore, biosorption using agricultural wastes offers an economical alternative to biological material. Heavy metal ions can be attached to these agricultural waste-based biosorbents due to functional groups such as carboxyl, hydroxyl, sulfhydryl, and amido (Kwikima et al., 2021).