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Preparation and Adsorption Properties of a Biosorbent from Banana Peel for Use as Natural Vitamin Beads in Cosmetic Products

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Abstract

The purpose of this research was to produce natural vitamin beads using a biosorbent from banana peel as an alternative to plastic vitamin beads for use in cosmetic products. The new biosorbents could be prepared by an extraction process in combination with a hydrothermal technique and physical processing. The biosorbent material has high fiber content, up to 45.25% by weight, particle sizes in the range of 10-160 µm, with a specific surface area of 21.5 m^2/g and a point of zero charge at pH 6.83. It has a high cellulose crystallinity index (I_{cr}) equal to 59.2%. It could be manufactured with a yield of 8.85%. The study on the adsorption equilibrium of this biosorbent material showed that the Langmuir isotherm fits better for the adsorption process (R^2 = 0.9912) than the Freundlich isotherm (R^2= 0.9532) which presented a monolayer surface adsorption mechanism confirmed by XRD of vitamin C from released solution. The biosorbent from banana peel has an effective adsorption capacity for vitamin C (5% solution) of 545 mg/g and the release efficiency of vitamin C was 80% in water. In addition, an increase of adsorption capacity from 27 to 50 °C showed that the adsorption reaction between the biosorbent and vitamin C was endothermic. We have concluded that biosorbent from banana peel can be prepared by a hydrothermal method that is energy-efficient and environmentally friendly. This biosorbent material can be used as a natural alternative to polyethylene beads for vitamin C release in cosmetic products for antioxidant effect. The product from this research is a new category that combines natural materials with active ingredients to be used in cosmetic applications to ensure health safety and environmental protection.

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Introduction

In the past few decades, people are increasingly paying attention to environmental impacts. Especially the problem of littering plastics into rivers, which affects the environment. Microplastics, which are extremely small plastic particles, may not be visible to the naked eye (smaller than 5 mm or 5,000 microns). They are used in households and industries such as vitamin beads and scrub beads in cosmetic products (NYS AOG, 2015). Microplastics contaminating water sources can affect the environment and the health of aquatic animals, for example, causing intestinal disorders of fish. In addition, the chemicals in microplastics can be toxic and threaten human health. Environmentalists therefore focus on solving the environmental problems caused by plastics, both relatively large (>5 mm) plastics called mesoplastics (Andrady, 2011) and microplastics (<5 mm) (Duis & Coors, 2016). There is an urgent need to develop biodegradable alternatives to plastics as sustained-release preservatives in cosmetics. In addition to solving problems by using various technologies and materials to treat wastewater, such as nanomaterials, polymers and green materials (Saleh, 2021), processes and products of environmentally friendly materials have been developed that are degradable such as natural materials to replace synthetic products (Jimenez et al., 2012). Plant cellulose is a very attractive natural material due to its outstanding adsorption and biodegradability properties (Bhasney et al., 2020).

Most natural fibers come from plants, with cellulose being the most abundant active ingredient. It is found in the cell walls of all plants. It plays a role in helping plants to be strong, solid and most importantly, insoluble in water. In nature, cellulose is often found in combination with lignin, hemicellulose, tannins, fats and pigments, etc. Cellulose is a natural fiber in plants that can be used extensively. It is a porous material that can be used as a filter material and a good biosorbent. Cellulose from fruits and vegetables is also used to make products that are safe to use and consume, such as ingredients in food to increase fiber content, as additives in cosmetics, etc. There are many fruits and vegetables that are commonly used to extract natural cellulose fibers for utilization, such as cellulose from rice husk (Yunus et al., 2019), corncobs (Garcia et al., 2022), banana pseudo-stem (Li et al., 2015; Nguyen et al., 2021), etc.

The selection of plant species and organelles with high fiber content is important for the preparation of the biosorbent. In addition, a fiber preparation method is necessary since other components such as proteins, lipids, carbohydrates, plant pigments and other soluble substances must be removed first through various fiber preparation processes. Fiber preparation methods are chemical extraction, mechanical processing and hydrothermal methods for efficient sorbent preparation (Shi et al., 2018; Phanthong et al., 2018). The hydrothermal method is one of the most efficient, energy-saving and environmentally friendly method (Tang et al. 2021) and is also convenient for scale-up in production from laboratory to semi-industrial and industrial scale.

Banana is a tropical fruit that is widely consumed around the world. It is found in tropical regions (Gowthaman et al., 2018), especially in Southeast Asia such as Thailand, Laos, Myanmar, Indonesia, Malaysia and Vietnam. It represents one of the most important fruit crops, with a global annual production of more than 50 million tons (Sharma et al., 2016). Banana is a fruit that can be consumed in both fresh form and used as an ingredient in many foods such as banana snacks, dried bananas and fried bananas (Mohapatra et al., 2010). Banana is also an economically important fruit for both domestic consumption and export, generating an annual income of more than 300 million baht (Singanusong & Sodchit, 2011). As a result, Thailand has a large amount of banana peels up to 200 tons per day that tends to increase continuously (Tibolla et al., 2018). Banana peels are generally littered. It was found that banana peels contain more than 53% of dietary fiber (Singanusong & Sodchit, 2011) and 15-17% of cellulose (Tibolla et al., 2018; Menon et al., 2017; Singanusong & Sodchit, 2011). Banana peels can be extracted as fiber for use in consumer products that are safe for health.

This project researched the preparation of cellulose fiber biosorbent from banana peels by a hydrothermal method, which is energy-efficient and environmentally friendly. The study focused on the adsorption efficiency of vitamin C by this biosorbent, which can be used as natural vitamin C beads instead of polyethylene beads in cosmetic products. The result of this research obtained a new type of product that combines natural materials with active ingredients to be used in cosmetic applications to ensure health safety and reduce plastic waste in water resources to protect the environment.

Materials and methods

1. Materials

"Hom Thong" banana peels were collected from King Fruit Company at Lamlukka, Pathum Thani Province, Thailand. The applied chemicals are sodium hydroxide (AR grade, from Ajax Finechem, Australia), potassium metabisulfite (AR grade, from Fluka, Switzerland), sodiumchlorite (AR grade, from Ajax Finechem, Australia), hydrogen peroxide (AR grade, from Qrec, New Zealand), ethanol (AR grade, from RCI Labscan, Thailand) and sulfuric acid (AR grade, from Qrec, New Zealand).

2. Preparation of biosorbent materials

The process of preparing biosorbent from banana peels is divided into three main processes starting from the banana peel pretreatment process. The next process is to isolate cellulose fibers by chemical processing. Finally, there is a process of reducing the size to microcellulose by a physical process. A summary diagram of the preparation process of biosorbent from banana peels is shown in Fig. 1 and consists of the following steps: Banana peels were extracted to isolate the active ingredient as the banana peel residues were prepared as dry coarse powder by a modified method of Chairgulprasert et al. (2013) for the preparation of biosorbent. The procedure was as follows: 1) Banana peels were prepared by separating the pulp and washing the peels with distilled water to remove dust and dirt. The banana peels were dried in the oven at 60°C for 12 hr, grinded with a high-speed blender to a coarse powder and placed in a refrigerator at 4°C before its chemical composition analysis by AOAC methods (2000). 2) The banana peel powder was extracted by soaking in 95% ethanol (in the ratio of 1:5 in w/v) for 24 hr to remove organic byproducts and the powder was dried in the oven at 60°C for 12 hr. 3) The banana peel powder was immersed in a solution of potassium metabisulfite (1% w/v) (in the ratio of 1:5 in w/v) for 12 hr. After that, the powder was filtered out, washed with distilled water and dried in the oven at 60°C for 12 hr. 4) The dry peel powder was weighed, ground, passed through a 40 mesh sieve and kept in a desiccator for further experiments.

The preparation of cellulose fibers from banana peel powder was chemically processed by a hydrothermal method in combination with the cellulose preparation method by Khawas & Deka (2016). The procedure was as follows: (1) The banana peel powder was mixed with 20% sodium hydroxide solution (in the ratio of 1:20 in w/v) and then filled in a hydrothermal reactor and heated at 100°C for 1 hr. The substance was filtered and washed with distilled water. (2) The resulting substance was dispersed in a 1% sodium chlorite solution (in the ratio of 1:20 in w/v) and the pH of the solution was adjusted to a value of 5. The mixture was placed in a hydrothermal reactor and heated to 80°C for 1 hr. The substance was filtered and washed with distilled water. (3) The resulting substance was added to a 5% potassium hydroxide solution and stirred at room temperature for 12 hr. The material was filtered and washed with distilled water. (4) The resulting substance was added to a 1% sulfuric acid solution (in the ratio of 1:20 in w/v) and then packed in a hydrothermal reactor to be heated at a temperature of 80°C for 2 hr. The substance was filtered and washed with deionized water to finally obtain cellulose as an adsorbent material from the banana peels.

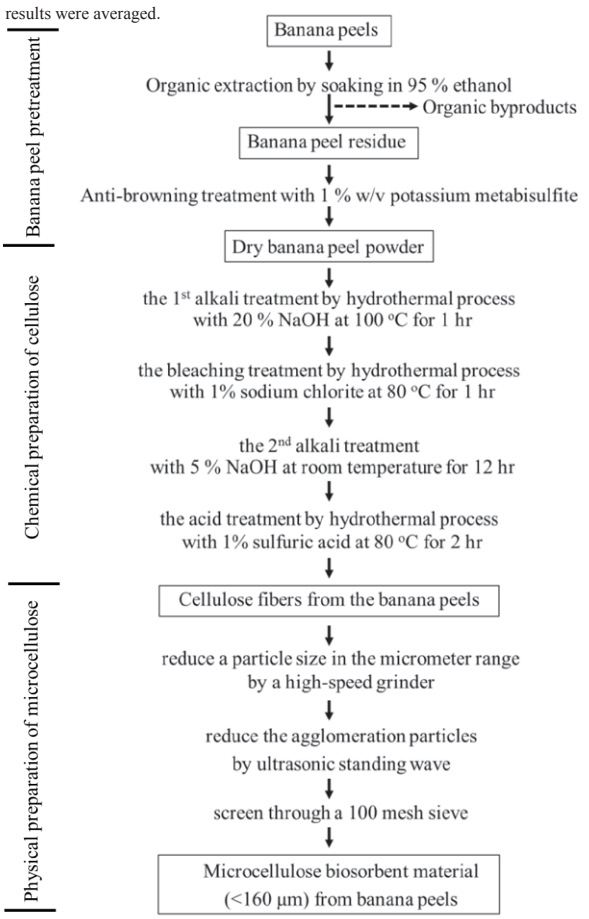

Fig. 1 Schematic diagram of the preparation of biosorbent from banana peels

Preparation of microcellulose from banana peels was done by a modified physical and mechanical process of Khawas & Deka (2016). The process was as follows: (1) The cellulose fibers from the chemically treated banana peels were reduced to a particle size in the micrometer range by a high-speed grinder. (2) The resulting substance was dispersed by ultrasonic standing wave in water for 30 min to reduce the agglomeration of the particles before drying. (3) Finally, the powder was screened through a 100- mesh sieve. The result was a microcellulose biosorbent material (<160 μm) made from banana peels. The biosorbent preparation experiment was repeated three times and the results were averaged.

3. Characterization and physical properties

3.1 Study the zero point charge of the biosorbent

The biosorbent prepared from banana peel was characterized by the point of zero charge (PZC; pH at the point of zero charge). Exact weights of 0.25 g of the prepared biosorbent material were added to beakers containing 50 mL buffer solution of pH 1-9, respectively. The mixtures were shaken at 250 rpm for 1 hr and then soaked for 24 hr. The mixture in each beaker was filtered and the pH was measured. The experiment was repeated three times, the measured pH values were averaged and the graph was plotted to determine the point of zero charge on the surface of the biosorbent material.

3.2 Surface analysis and characterization

The specific surface area of the biosorbent prepared from banana peel was analyzed by the BET method using a surface analyzer (BET), Model CIEX/X500RAnton.

The surface morphology of the biosorbent was characterized by scanning electron microscope (SEM: JSM-7610F, Oxford). The sample was fixed on 10 mm diameter aluminum stubs with double-sided tape and coated with a fine layer of gold using a sputter gold coater to improve conductivity. The surface characteristic of the coated samples were scanned under 1000x magnification.

3.3 X-ray diffraction (XRD)

X-ray powder diffraction profiles of the biosorbent were collected by a Bruker diffractometer, Model D8 Advance at ambient temperature, using Cu Kα radiation (λ = 0.15418 nm) with operating voltage and current of 40 kV and 30 mA, respectively. The diffraction intensities were recorded between the 2θ angle range of 5 and 50° with a scanning speed of 0.5°/min. The crystallinity index (I_{cr},%) of the biosorbent was calculated using equation (1), following the method of Segal et al. (1959).

$$I_{cr} = \frac{I_{002} - I_{am}}{I_{002}} \; x \; 100 \qquad \text{.....(1)}$$

With I_{cr} The crystallinity index

I_{002} The maximum intensity of diffraction corresponding to the 002 plane of cellulose crystals (diffraction intensity close to 2θ at 22°)

I_{am} The intensity of diffraction referring to amorphous cellulose (diffraction intensity close to 2θ at 18°)

The crystallinity index was used to describe the relative amount of crystalline cellulose in the biosorbent; the crystallinity percentage was calculated as the ratio of heights between the maximum intensity of the crystalline diffraction and the intensity of the non-crystalline (amorphous) diffraction materials.

3.4 Fourier-transform infrared spectroscopy (FTIR)

The functional groups of the biosorbent were analyzed by adsorption spectroscopy using a Fourier Transform Infrared Spectrophotometer (IR Tracer- 100, SHIMADZU, Japan). The samples were prepared by using the KBr disk (ultra thin pellets) technique with a pellet preparation as a carrier of the dry sample in the ratio of 1:100. IR spectra of samples were measured within the infrared region between 4000 and 400 cm^{-1}, with a resolution of 4 cm^{-1} and 20 scans.

4. Batch adsorption studies

To study the effect of concentration and contact time for the adsorption of Vitamin C on the surface of the biosorbent material, exact amounts of 0.25 g of the biosorbent were added into different Erlenmeyer flasks. Vitamin C solutions at concentrations of 0.50, 1.00, 2.00, 3.00, 4.00 and 5.00% w/v were added to 50 mL of the flasks. The solutions were shaken by a shaker (n-biotek, NB-205) at a speed of 120 rpm at 27°C with different periods of 0, 1, 3, 5, 10, 15, 30, 60, 120 and 180 min, respectively. The flasks were then removed from the shaker and the solutions filtered through filter papers to separate the biosorbent from the solutions. The final concentration of Vitamin C in the solutions was analyzed by a double beam UV-Visible Spectrophotometer (Shimadzu, UV-2401PC). The experiment was repeated three times and the results were averaged.

To study the effect of concentration and temperature for the adsorption of Vitamin C on the surface of the

biosorbent, exact amounts of 0.25 g of the biosorbent were added into different Erlenmeyer flasks. 50 mL of different concentrated solutions of vitamin C (0.50, 1.00, 2.00, 3.00, 4.00 and 5.00%w/v) were added to each of the flasks. Each sample was kept in a shaker at temperatures of 27 and 50°C for equilibrium time (120 min). The final concentration of Vitamin C in the solutions was analyzed by a double beam UV-Visible Spectrophotometer (Shimadzu, UV-2401PC). The experiment was repeated three times and the results were averaged. The adsorption capacity of vitamin C at equilibrium, q_e was calculated by equation (2).

$$q_e = \frac{(C_0 - C_e)V}{W} \qquad \text{.....(2)}$$

With q_e as adsorption capacity of vitamin C at equilibrium (mg/g)

C_0 is the initial concentration of the vitamin C solution (mg/L)

C_e is the equilibrium concentration of the vitamin C solution (mg/L)

V is the volume of the vitamin C solution (L)

W is the weight of the biosorbent (g)

5. Study the amount of desorption of vitamin C from the biosorbent

To study the efficacy of the release of vitamin C from the surface of biosorbents into water, exact amounts of 0.25 g of the biosorbent, which had adsorbed vitamin C in a solution with a concentration of 1.0%w/v, were added into Erlenmeyer flasks. 50 mL distilled water was added to each flask and shaken at 27°C for 0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80 and 90 min, respectively. The amount of vitamin C which was released from the biosorbent was determined by a UV-Visible Spectrophotometer (Shimadzu, UV-2401PC). The experiment was repeated three times and the results were averaged.

Results and discussion

1. The preparation of biosorbent from banana peels

The ethanol extracted, crushed banana peel powder samples were treated to inhibit enzymatic browning by soaking in 1% potassium metabisulfite (anti-browning agent) solution at room temperature for 12 hr and drying at 80°C for 12 hr (Arora et al., 2018). The dry peel powder was weighed, ground and passed through a 40 mesh sieve. The resulting substance was banana peel coarse powder used for the preparation of biosorbent materials.

Chemical preparation of cellulose from banana peel powder by the method of Khawas & Deka (2016) combined with a hydrothermal method was performed. The chemical process is described as follows: Step 1 is the 1st alkali treatment. Sodium hydroxide was used to hydrolyze and solubilize pectins, starch, hemicelluloses and proteins. Step 2 is the bleaching treatment. Sodium chlorite solution was used to remove phenolic compounds and molecules with chromophoric groups (coloring groups). Most of the lignin was bleached by the rapid oxidation by chlorine and chlorite. As a result of this reaction, hydroxyl, carboxyl and carbonyl groups were generated, which contributed to greater solubility of lignin in alkali (Dufresne et al., 1997). Step 3 is the 2nd alkali treatment. Potassium hydroxide was used to remove other contaminants dissolved in alkali. Step 4 is the acid treatment. Sulfuric acid was used to remove residual pectin and to break down large fibers (digestion of bigger fibers). The resulting cellulose product consisted of white fine, small fiber material.

Physical preparation of microcellulose from banana peel cellulose included milling in a high-speed grinder to reduce the particle size of the fibers. The cellulose product was dispersed with an ultrasonic machine to fine-tune and shrink the fibers. It was found that the use of ultrasonic waves produces strong mechanical vibrations in which liquid molecules adsorb the energy of sound waves, expanding them into bubbles and forming cavitations. The resulting shock wave can separate the fibers or agglomerating particles. The resulting microcellulose was a white fine powder with a particle size < 160 μm.

The yield analysis of the microcellulose product as biosorbent showed that the percentage yield was 8.85.

2. Chemical Composition

The chemical composition of the biosorbents compared to the chemical composition analysis of dried banana peels (raw materials) are shown in Table 1. It was found that the highest part of dried banana peels were carbohydrates with 62.05% of total weight, followed by fiber content 13.54%, moisture 8.32%, ash 8.12%, protein 4.01% and fat 3.96%, respectively. In comparison, the biosorbent contained a lower carbohydrate composition (44.85%) and had a high fiber content, up to 45.25% by weight. This was less than the 72.36% fiber content of

commercial cellulose (Singanusong & Sodchit, 2011). However, the result of the research is that the preparation of cellulose from natural materials yields relatively high fiber content. This is the reason why banana peel fibers have the potential to be used as a natural adsorbent.

Table 1 Chemical Composition

Composition	Content (%)	
	Dried banana peel	Biosorbent from banana peel
Moisture	8.32 ± 0.05	4.05 ± 0.10
Fat	3.96 ± 0.48	1.56 ± 0.25
Protein	4.01 ± 0.45	2.28 ± 0.13
Carbohydrate	62.05 ± 0.12	44.85 ± 0.10
Ash	8.12 ± 0.54	2.01 ± 0.68
Fiber	13.54 ± 0.15	45.25 ± 0.47

Remark: Results are mean ±SD of triplicate analysis

3. Characterization and physical properties of the biosorbent

3.1 Point of zero charge of biosorbent

The analysis of the charge on the surface of the biosorbent is shown in Fig. 2. The two curves intersect at a pH of 6.83 indicating that the biosorbent has a zero point charge equal to 6.83. A pH value less than 6.83 will result in a positive charge due to the amount of hydronium ions (H_3O^+) on the surface of the biosorbent. Hydroxide ions (OH^-) ions at a pH greater than 6.83 will cause negative charges (Bharathi & Ramash, 2013).

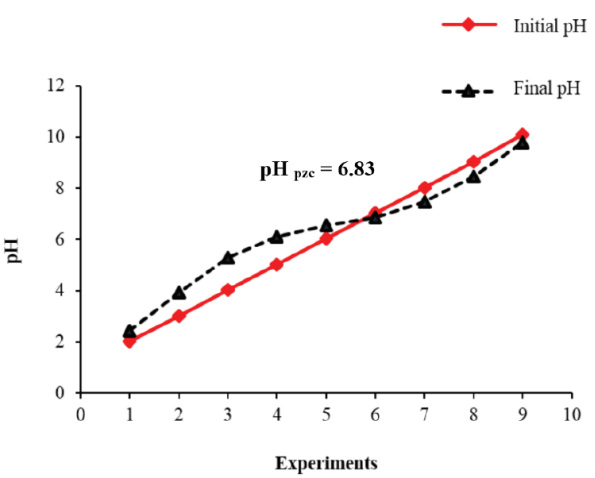

Fig. 2 Point of zero charge of biosorbent from banana peel: (◆) solid red line is initial pH and (▲) black dashed line is final pH

3.2 Specific surface area

The results of the analysis of the specific surface area of banana peels compared with the biosorbent material produced from banana peel revealed that the specific surface area of the biosorbent was 21.5 m^2/g which is substantially greater than the specific surface area of banana peels (15.7 m^2/g). The results were similar to the surface area of the natural cellulose (5.3-28.1 m^2/g) (Constant et al., 2016). However, the specific surface area of the biosorbent from banana peel was less than that of activated carbon produced from banana peel (311.18-625.82 m^2/g) (Wanprakhona et al., 2021).

3.3 Scanning electron microscopy

The morphological results of banana peel surfaces and biosorbent material produced from banana peels by scanning electron microscope (SEM) are shown in Fig. 3. It revealed that the microstructure of the banana peel surface was significantly different from the surface of the biosorbent. The surface of the banana peel (Fig. 3a) was irregular and had layers of deposits due to the presence of several components: carbohydrates, proteins, lipids, lignins, pectins, cellulose and hemicellulose (Li et al., 2015). In contrast, the surface

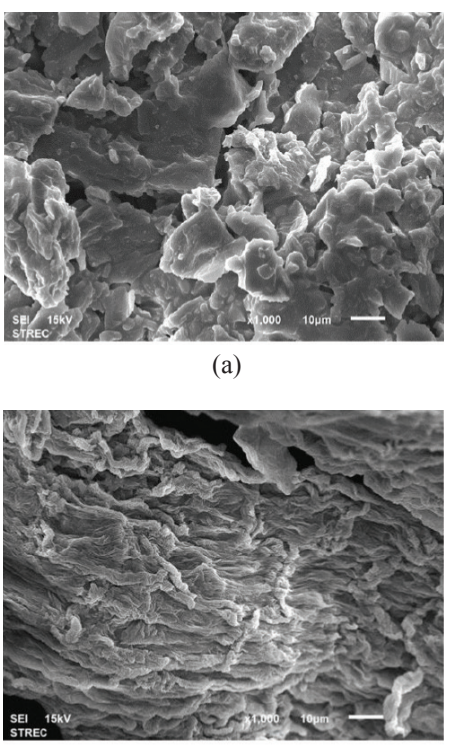

Fig. 3 SEM images of (a) banana peel and (b) biosorbent prepared from banana peel at magnification of 1000x

of the biosorbent (Fig. 3b) was uniform, smooth and clean, due to the non-fibrous constituents removed by the chemical pretreatment. It was also found that the chemical treatment helped in the removal of some amorphous components such as lignin, pectin and hemicelluloses (Pelissari et al., 2014).

3.4 Fourier transform infrared spectroscopy (FT-IR)

The results of the functional group determination of the material using Fourier transform infrared-spectroscopy (FTIR) technique to analyze the lignin, cellulose and hemicellulose composition of untreated banana peels were compared with the cellulose fiber composition of the biosorbent. The study was conducted in the wave number range between 400 and 4000 cm^{-1}.

The FTIR spectrum of untreated banana peels (Fig. 4) showed a broad vibrational band at wave number 3650–3000 cm^{-1}, corresponding to the stretching and bending modes of the hydroxyl (-OH) groups on the surface. Peaks at wave number 2950-2850 cm^{-1} showed asymmetric C-H stretched vibrations involving lignin and hemicellulose. Signals at wave numbers 1040-1020 cm^{-1} corresponded to stretching vibrations of C-O-C in the pyranose ring consistent with the cellulose composition. The peak at wave number 1730 cm^{-1} showed stretching vibrations of the C-O bonds of acetyl and ester in lignin, hemicellulose pectin. A peak at wave number 907-897 cm^{-1} was related to the β- bond glycosidic in cellulose and a peak at wave number 897 cm^{-1} indicated cellulose I.

The FTIR spectrum of the biosorbent prepared from banana peel (Fig. 5) showed decreased intensity of vibrational bands at wave number 2950-2850 cm^{-1}. The bands at wave number 1040-1020 cm^{-1} associated with the stretching bond of C-O-C in the pyranose ring clearly represent cellulose. The intensity of the stretching vibrational peak of C-O at wave number 1730 cm^{-1} was reduced because the hemicellulose and lignin components were eliminated in the chemical process. The vibrational bands at wave number 907-897 cm^{-1} showed a decrease in intensity after chemical treatment, indicating that lignin was removed.

3.5 X-ray diffraction (XRD)

A X-ray powder diffraction analysis of banana peel and biosorbent was performed, with XRD patterns shown in Fig. 5. It was found that the diffractogram of banana peel (Fig. 6a) displayed an amorphous characteristic. It shows a peak at 2θ = 17°, indicating a typical B-type pattern of starch (Tibolla et al., 2018). In comparison, the diffractogram of biosorbent from banana peels (Fig. 6b) showed X-ray diffraction peaks of 2θ angles at 16° and 22°, which are characteristic of cellulose I crystals with parallel structures (Yiying et al., 2015).

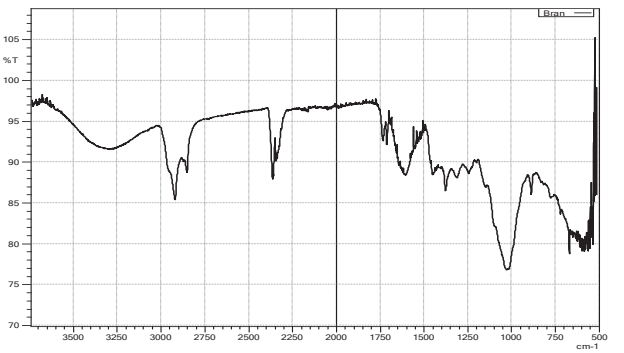

Fig. 4 FTIR spectrum of untreated banana peels

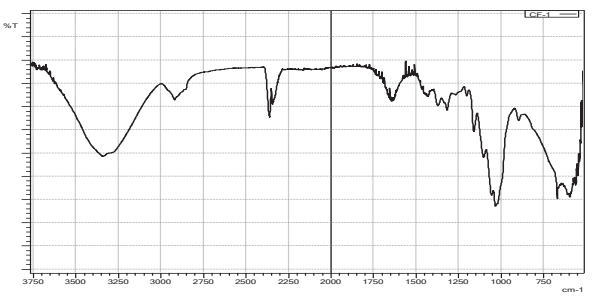

Fig. 5 FTIR spectrum of the biosorbent prepared from banana peel

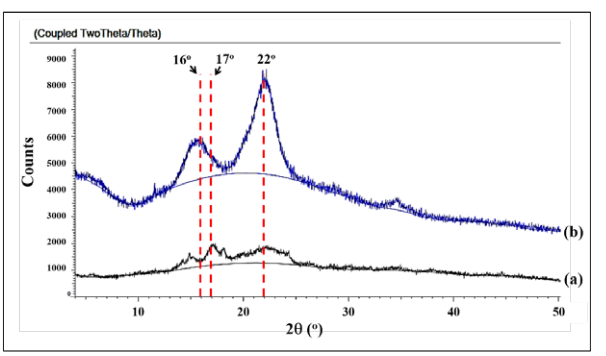

Fig. 6 XRD patterns showing amorphous characteristic of (a) banana peel and (b) cellulose I of biosorbent prepared from banana peels

X-ray diffraction peaks around 2θ =16° and 22° refer to 101 and 002 plane positions that are characteristic for cellulose. The crystallinity index (I_{cr},%) of banana peel and biosorbent was determined by equation (1) of Segal et al. (1959). The result showed that banana peel (raw material) had a low crystallinity index (I_{cr} = 11.1%) as amorphous material, while the

biosorbent showed a very high crystallinity index (I_{cr} = 59.2%). This value was higher than the prepared cellulose by alkaline treatment (I_{cr} = 36.6%) (Madhushani et al., 2020), mechanical extraction (I_{cr} = 50.8%) (Madhushani et al., 2020) and the natural cellulosic fibers derived from Senna auriculata for making light weight industrial biocomposites (I_{cr} = 49.6%) (Nagarajaganesh et al., 2019). In contrast, our result was lower than prepared nanocellulose by different methods such as enzymatic treatment (I_{cr} = 66.2%) (Tibolla et al., 2018) and NaOH/HNO_3-$NaNO_2$ oxidation (I_{cr} = 80.1%) (Kumar et al., 2019)

4. Adsorption of biosorbent from banana peel

4.1 Effect of contact time

The effect of contact time for the adsorption of vitamin C by the biosorbent is shown in Fig. 7. In the beginning the graph is very steep and became parallel to the x-axis later at equilibrium time. That means a large amount of vitamin C was adsorbed rapidly during the initial 15 min of contact and then the adsorption speed slowed down until equilibrium was achieved. The rapid initial adsorption could be attributed to the large amounts of adsorbent active sites available for adsorbate molecules (Ahmad & Kumar, 2010).

In the early start time, the biosorbent can adsorb vitamin C quickly because of a high surface area available for adsorption until the equilibrium time at 30 min when the active sites are saturated with vitamin C molecules.

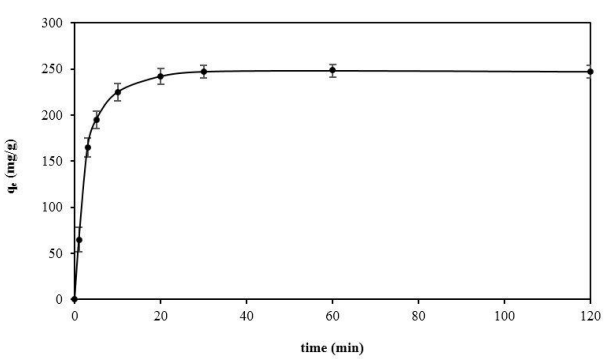

Fig. 7 Effect of contact time for the adsorption of vitamin C on biosorbent from banana peels (solution pH 7, temperature 27 °C). Data points are the mean of the results of three replicates and error bars show standard deviation

4.2 Effect of concentration

In the present study, the concentration of vitamin C solutions varied from 0.50, 1.00, 2.00, 3.00, 4.00 and 5.00% w/v. The effect of the concentration on the amount adsorbed is shown in Fig. 8; the adsorption capacity of the biosorbent increased steadily when the vitamin C concentration increased up to 5.0% w/v indicating higher amounts of vitamin C molecules occupy the surface of the biosorbent at higher concentrations (Ahmad & Kumar, 2008).

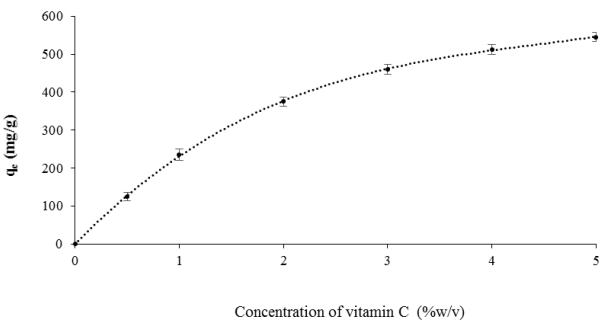

Fig. 8 Effect of concentration for the adsorption of vitamin C on biosorbent from banana peels. Data points are the mean of the results of three replicates and error bars show standard deviation

4.3 Effect of temperature

Table 2 and Fig. 9 show the effect of temperatures on the adsorption of biosorbent from banana peels at two different values (27 and 50°C). When the temperature raises, the biosorbent can adsorb more vitamin C at all tested concentrations due to higher kinetic energy, so more adsorbate molecules can move onto the surface of the adsorbent (Aksu et al., 2008). This result is similar to the methylene blue adsorption behavior of microcrystalline cellulose from banana pseudo-stem (Nguyen et al., 2021). This indicates that the adsorption of vitamin C on the surface of the biosorbent from banana peels is an endothermic process (Ahmad & Kumar, 2010).

Table 2 Effect of temperature for the adsorption of vitamin C on biosorbent from banana peels at temperatures of 27°C and 50°C

Concentration of vitamin C (% w/v)	q_e (mg/g)	
	27 °C	50 °C
0	0	0
0.5	125	179
1.0	247	312
2.0	390	450
3.0	463	545
4.0	512	602
5.0	545	650

Remark: Results are mean of triplicate analysis

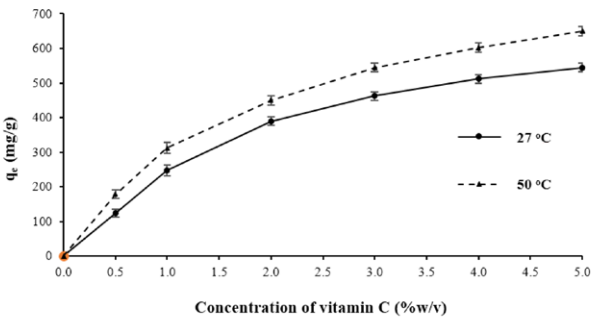

Fig. 9 Effect of temperature for the adsorption of vitamin C on biosorbent from banana peels at different temperatures: (●) 27°C and (▲) 50°C. Data points are the mean of the results of three replicates and error bars show standard deviation

4.4 Adsorption Isotherm

Adsorption isotherms shows the relationship between the amounts of vitamin C adsorbed per unit weight of biosorbent at constant temperature. The adsorption behavior of vitamin C on the biosorbent can be described by Langmuir and Freundlich isotherms as in equation (3) and (4), respectively.

$$\frac{1}{q_e} = \left(\frac{1}{q_{max} K_L C_e}\right) + \left(\frac{1}{q_{max}}\right) \qquad \text{.....(3)}$$

$$\log q_e = \log K_F + \left(\frac{1}{n} \log C_e\right) \qquad \text{.....(4)}$$

When q_e is the equilibrium loading of adsorbate per unit mass of adsorbent (in mg/g)

C_e is the equilibrium concentration of vitamin C solution (mg/L)

q_{max} is the maximum adsorbed vitamin C amount on monolayers (mg/g)

K_L is the Langmuir constant related to adsorption capacity (mg/L)

1/n is the adsorption constant (strength of adsorption) (mg/g)

K_F is the Freundlich constant related to rate of adsorption (mg/g)

The adsorption isotherms of vitamin C adsorbed on the biosorbent are shown in Fig. 10 and 11 for the Langmuir and Freundlich mechanism, respectively. The adsorption isotherm is important to describe how the adsorbate interacts with the adsorbent. It was found that the correlation coefficient (R^2) of the Langmuir isotherm came closer to 1 than the Freundlich isotherm. That means the adsorption behavior of vitamin C on the biosorbent corresponds slightly better with the Langmuir than the Freundlich isotherm. It presents a monolayer surface adsorption mechanism without dissociation of vitamin C and confirmed by XRD of vitamin C from the released solution. Therefore, the behavior of vitamin C molecules is best described as a monolayer adsorption process on the surface of biosorbent from banana peels (Bharathi & Ramash, 2013). This adsorption isotherm is similar to the adsorption of methylene blue in aqueous solutions by biosorption from waste biomaterial (Chowdhury & Saha, 2012) and the adsorption of methyl orange (MO) of asphaltene (Siddiqui, 2017). All of them are adsorption of organic adsorbents with organic sodium salts adsorbates. This corresponds to the adsorption mechanism with weak intermolecular interactions such as electrostatic attraction and hydrogen bonding (Olivito et al., 2021).

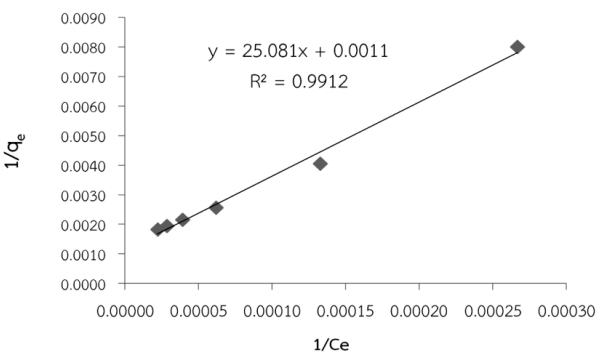

Fig. 10 The correlation curve according to Langmuir adsorption isotherm of vitamin C adsorption by biosorbent from banana peels

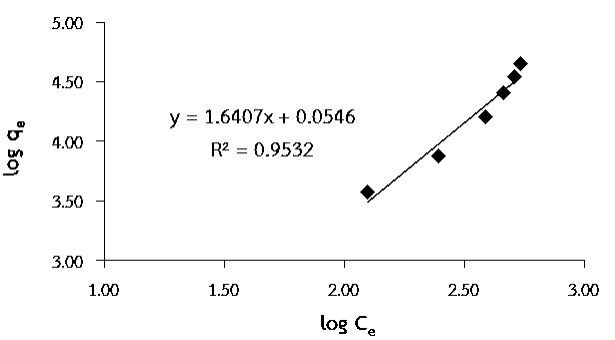

Fig. 11 The correlation curve according to Freundlich adsorption isotherm of vitamin C adsorption by biosorbent from banana peels

5. Desorption of vitamin C from the biosorbent

To study the release of vitamin C in the presence of water as a solvent, different time intervals (0 - 90 min) at constant temperature of 27°C were chosen. It was found that the biosorbent (vitamin C bead from banana

peel) can release vitamin C in an amount equal to 200 milligrams (80%) per gram of biosorbent from a total of 247 mg/g (Fig. 12).

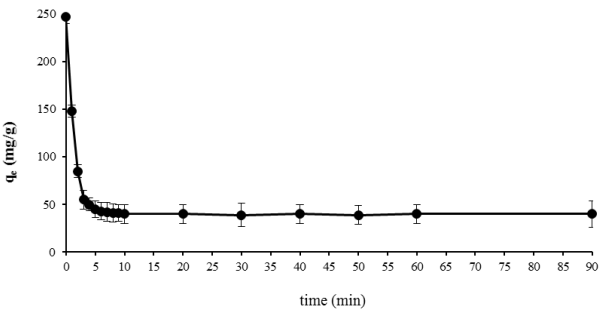

Fig. 12 Effect of contact time for the release of vitamin C from the biosorbent from banana peels. (at temperature of 27 °C). Data points are the mean of the results of three replicates and error bars show standard deviation

The results of a study on the release of vitamin C from vitamin beads from banana peels by analyzing the X-ray diffraction of the dried powder of the substance as released from the vitamin beads. The results are shown in Fig. 13. The XRD pattern of vitamin C (Fig. 13c) confirms the vitamin C release of the beads from banana peels.

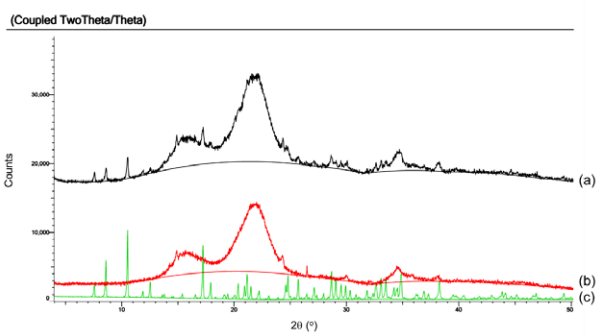

Fig. 13 X-ray diffraction patterns of (a) Vitamin C beads from banana peels (b) Residue from release (c) Vitamin C released from the vitamin beads

A comparison of the applications of biosorbent vitamin C beads prepared from banana peels and commercial polyethylene vitamin C beads for cosmetic products revealed that: The biosorbent vitamin C beads contained 247 mg/g of adsorbent (prepared with 0.25 g of the biosorbent adsorb vitamin C in a solution with a concentration of 1.0%w/v) have a release efficacy of vitamin C (200 mg/g of biosorbent) similar to commercially available polyethylene capsule beads (Vitamin C solution with the concentration of 250 mg/mL, T.P. Drug Laboratories (1969) Co., Ltd.), but differ in the release mechanism. Vitamin C beads prepared from banana peels have a mechanism that gradually releases vitamins from the biosorbents by rubbing, so the use of beads from banana peels is not likely to cause allergic reactions or irritation from the concentrated active ingredient. In contrast, vitamins in polyethylene beads have a single release mechanism of the concentrated active ingredient by bursting the beads. Therefore, these biosorbents are more suitable for use in massaging cosmetic products such as massage creams or gels than for use in liquid products. However, environmental safety is an important aspect which should be realized along with the benefits. Vitamin beads prepared from banana peels consist mainly of natural cellulose fibers from waste material which are degradable in the environment, while polyethylene vitamin beads contain microplastics that are harmful to the environment and are banned for usage globally (Habib et al., 2022).

Conclusion

Banana peel is a waste material from banana product processing that can be used to prepare a microcellulose biosorbent. Physical combined with chemical processes using hydrothermal techniques to improve extraction efficiency saves energy consumption and environmentally friendly methods were used in the preparation of a biosorbent from banana peels with a yield of 8.85%. The adsorption equilibrium of vitamin C by the biosorbent corresponds to a Langmuir isotherm ($R^2 = 0.9912$). Microcellulose biosorbents from banana peels could be used as natural vitamin beads that could store up to 500 mg of vitamin C per gram of banana peel adsorbents. The efficiency of vitamin C release was 80%. However, the safe use of products obtained from this study as ingredients in natural cosmetic products should take into account the regulatory dosage of the active ingredient. A suggestion for further research is a hydrothermal extraction technique to prepare biosorbent from banana peel, in addition to exploring its advantages in terms of energy saving, use of chemicals and controlled emissions into the environment. There is also the potential to collect waste from the process in order to extract by-products such as lignin that provides added value to the process.

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