Betel Nut Peel Powder as Biosorbent for Mg(II), Ca(II), and Fe(III) in Agricultural Water

Carissa Ayu Susiana[1], Feri Mukhayani[1], Erwinton Simatupang[2], Fajar Inggit Pambudi[1], I Wayan Sumerta[2], Guntur Mulyanegara[2], Mohammad Nur Samudin[2], Dedo Kevin Prayoga[2], and Nuryono Nuryono[1*]

[1]*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada,*
Sekip Utara, Yogyakarta 55281, Indonesia

[2]*PT. Pertamina EP Pendopo, Jl. Plaju No. 38 Komperta Pendopo, Talang Ubi Kab. Penukal Abab Lematang Ilir (PALI),*
South Sumatera 31211, Indonesia

* ***Corresponding author:***

email: nuryono_mipa@ugm.ac.id

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Abstract: *Water pollution from heavy metal contamination is a global issue; thus, finding low-cost and sustainable solutions is challenging. Among various methods, biomass adsorption is a practical approach for treating heavy metal contamination in agricultural water. This study explored the use of betel nut peel as a biosorbent to remove Mg(II), Ca(II), and Fe(III) ions from agricultural water. The adsorbent contained active groups like O–H, C=O, and C=C, indicating cellulose, lignin, and hemicellulose compounds. Mature betel nut peels showed higher adsorption capacities than immature ones due to their larger surface area and more active sites. The optimal adsorption occurred at an initial adsorbate concentration of 100 mg L^{-1} for 1 h, with 5 mg of biosorbent. The biosorbent followed the Langmuir isotherm and a pseudo-second-order kinetic model ($R^2 = 0.99$), indicating chemisorption. When applied to agricultural water from South Sumatra, the biosorbent removed up to 90% of Fe(III) ions. These findings suggest that betel nut peel powder has strong potential as a biosorbent for heavy metals, with promising applications in water treatment and environmental remediation. It also shows potential as a biofertilizer, particularly for soils rich in Fe(III).*

Keywords: *betel nut peel; biosorbent; metal ions; agricultural water*

■ INTRODUCTION

Environmental pollution caused by heavy metals is a growing global issue. The rising waste from mining and agrochemical industries plays a major role in environmental contamination, particularly in agricultural waters. These wastes contain pollutants, including heavy metal ions such as cadmium, copper, iron, magnesium, and calcium [1]. Water, soil, and air are all adversely affected by these wastes, both directly and indirectly. Vegetation, livestock, and humans are also impacted. Agricultural soil and water are particularly vulnerable to contamination [2]. Metal ions in the soil can infiltrate groundwater, leading to their accumulation at harmful concentrations, which pose health risks such as carcinogenic effects, morphological abnormalities, high mortality, and mutagenic effects in humans [3]. Additionally, high levels of heavy metals in soil can reduce fertility, further deteriorating the quality of agricultural crops. As heavy metal ions are non-biodegradable and persistent, their accumulation in soil must be addressed urgently to prevent long-term environmental damage.

The mobility of heavy metal ions in the soil should be minimized to prevent these pollutants from reaching groundwater. Several conventional methods have been used to remove contaminants from water, including adsorption, chemical precipitation, oxidation, reverse osmosis, filtration, coagulation/flocculation, ozonation, membrane processes, electrocoagulation, ion exchange, and liquid-liquid extraction [4-5]. Among these techniques, adsorption has emerged as one of the most effective methods in separation technology, particularly in wastewater treatment. Adsorption is favored due to its simplicity, high separation efficiency, low energy consumption, and ability to target pollutants even at low concentrations [6-7].

Commercial activated carbon is widely used in heavy metal wastewater treatment; however, its application is limited due to high production costs and challenges in regeneration. To address this, biomass-based adsorbents (biosorbents) have gained attention as cost-effective alternatives. However, previous research has shown that biosorbents face certain limitations, such as low adsorption capacity and poor selectivity for specific heavy metals in complex aqueous environments [8-9]. Moreover, the performance of these biosorbents, such as betel nut peel, can be affected by factors like pH, temperature, and the presence of competing ions, reducing their effectiveness in treating real-world wastewater samples [10].

This study explores the use of betel nut (*Betel catechu* L.) peel powder as a biosorbent for Mg(II), Ca(II), and Fe(III) metal ions in rice field water in South Sumatra. Betel nut (*Areca catechu* L.) is a major agricultural export commodity commonly found across Sumatra, Kalimantan, Sulawesi, and Nusa Tenggara. Currently, betel nut plants are mainly limited to the fruit and seeds used in herbal medicine mixtures and as raw materials for the pharmaceutical industry [11]. The remaining betel nut peels are typically discarded as solid waste, contributing to environmental pollution. Research has shown that betel nut peel contains significant chemical compounds, including cellulose (63.20%), hemicellulose (32.98%), lignin (7.20%), and fat (0.64%) [12]. The high cellulose content in betel nut peel makes it a practical, low-cost adsorbent for reducing metal contamination. These metals, including Mg(II), Ca(II), and Fe(III), are critical to agricultural water due to their roles as essential nutrients for plant growth. Mg and Ca are vital macronutrients that help maintain plant health and structure, while Fe is crucial in photosynthesis and overall plant metabolism. However, excessive concentrations of these ions, especially in hard water, can negatively affect plant growth and soil quality. These metals also include macronutrients (K, Na, Mg, and Ca), micronutrients or trace elements (Ni, Fe, Mn, Co, Cu, Zn, and Mo), and non-essential or heavy metals such as Hg, Pb, Cd, Sn, and Ag [1]. The presence of Mg(II), Ca(II), and Fe(III) ions in Indonesian agricultural water, particularly in areas with hard water, as well as Fe(III) contamination from rusting iron pipes in the Pertamina Industry Pendopo Field, highlights the need for effective remediation.

This study examined the effectiveness of both immature (P1) and mature (P2) betel nut peels as biosorbents, focusing on their pore characteristics and active sites [12]. Betel nut peel powder offers distinct advantages over other biosorbents due to its rich content of functional groups, especially hydroxyl groups (O−H), which enhance its ability to adsorb metal ions [13]. These hydrophilic groups, along with cellulose, make betel nut peel powder highly effective in binding metal ions such as Mg(II), Ca(II), and Fe(III). These properties provide a sustainable, cost-effective solution for wastewater treatment, especially in agricultural areas. Compared to other biosorbents, betel nut peel powder has the potential for large-scale applications due to its availability, low cost, and efficiency in metal ion removal. To evaluate its effectiveness, a batch adsorption study was conducted to determine the optimal parameters (biosorbent dosage, initial adsorbate concentration, and contact time) for adsorbing Mg(II), Ca(II), and Fe(III) ions. These optimal conditions were applied to adsorb heavy metal ions from rice field water samples.

■ EXPERIMENTAL SECTION

Materials

Immature (2 months old) and mature (4 months old) betel nuts were collected from the plantation area in Sukakarya Village, Musi Rawas Regency, South Sumatra. A multi-element stock solution was prepared by dissolving known masses of nitrate salts of analytical grade, including $Fe(NO_3)_3{\cdot}9H_2O$, $Ca(NO_3)_2{\cdot}4H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ sourced from Merck, Germany. Distilled water was used as the solvent. The soil samples were taken from two locations in Sukakarya Village, Musi Rawas Regency, South Sumatra. The first sample (negative control) was soil collected from the rice paddy field that was not fertilized with nut peel compost. The second sample (positive control) was taken from the field that had been fertilized with compost fertilizer for 1 year. Each sample was taken approximately at a depth of 10–20 cm.

Instrumentation

In this study, the samples were characterized using X-ray fluorescence (XRF, NEX QC+ Quantez) to determine their elemental composition. Attenuated total reflectance-infrared (ATR) spectroscopy (NICOLET, Is10 Thermo Fisher Scientific) was employed to identify functional groups in the 600–4000 cm^{-1} frequency range. The morphology and elemental distribution were observed through scanning electron microscopy with energy-dispersive X-ray (SEM-EDX, JEOL JSM-6510LA), operating at 5 kV and 30 mA. The concentrations of Mg(II), Ca(II), and Fe(III) ions were analyzed using an atomic absorption spectrophotometer (AAS, Perkin Elmer 3110).

Procedure

Sampling area

P1 and P2 betel nuts were collected from the plantation area in Sukakarya Village, Musi Rawas Regency, South Sumatra. The betel nuts were then peeled, and the peel was separated. The peels were washed thoroughly and sun-dried for 4 d (from 8 a.m. to 4 p.m.). Once dried (Fig. 1), the betel nut peels were ground into powder. The resulting powder was used directly without any further treatment.

Two agricultural soil samples were collected from rice fields in Sukakarya Village, Musi Rawas Regency, South Sumatra. One sample was taken from a rice field that had been fertilized with betel nut peel, while the other sample was from a field that had not received betel nut peel fertilizer. The soil samples were obtained from a depth of 20–30 cm and stored in polypropylene containers. The soils were then dried and homogenized in the laboratory. The pH of both soil samples, mixed with water in a 1:1 (w/w) ratio, was measured.

In addition to the soil samples, two different water samples were collected from the same area as the soil samples to test the effectiveness of the biosorbent. Groundwater (W1) was collected near the paddy water (W2) sampling area, approximately 300 m away, as the control. The paddy water samples were taken from the rice field area where betel nut peel compost was regularly applied every 3 months.

Adsorption experiment

Before use, the betel nut peel powder was sieved through a 100-mesh sieve. Batch adsorption experiments for single-component systems were conducted by stirring a specific amount of betel nut peel powder in 20 mL of

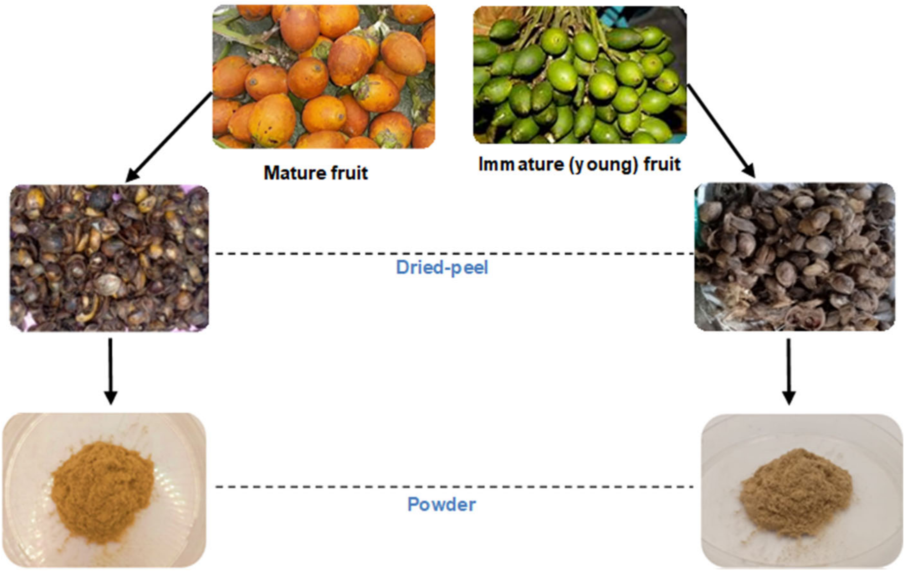


Fig 1. Dried peels of mature (P2) and immature betel nut peels (P1)

the metal ion solution being tested. An automatic stirrer was used at an optimal speed of 100 rpm. After the adsorption process, the adsorbent was filtered using filter paper. The metal ion concentration in the filtrate was then measured using AAS.

Adsorption kinetics study

The adsorption kinetics study was performed by adding betel nut peel powder (with biosorbent doses varying from 1, 5, 10, 15, and 20 mg) into 20 mL of $Fe(NO_3)_3$, $Ca(NO_3)_2$, and $Mg(NO_3)_2$ solutions in glass bottles. The solution was stirred for 15, 30, 60, 90, and 120 min. Afterward, the filtrate was separated and analyzed for the concentration of residual metal ions. Additionally, the effect of initial concentration on the adsorption of Mg(II), Ca(II), and Fe(III) metal ions was investigated using 20 mg of biosorbent with varying concentrations at room temperature. The solution was filtered after stirring for 60 min, and the adsorption isotherms were assessed at these concentrations.

Data processing

The number of metal ions adsorbed at equilibrium, i.e., q_e (mg g^{-1}), was calculated using Eq. (1):

$$q_e = \frac{(C_0 - C_e)V}{M} \tag{1}$$

where C_0 and C_e represent the initial concentration of metal ions and the concentration at equilibrium of the metal in the liquid phase (mg L^{-1}), respectively; V is the volume of the solution in liters (L); and M is the mass or dose of biosorbent used.

The sorption equilibrium data were analyzed using the Langmuir and Freundlich adsorption isotherms. The Langmuir isotherm quantitatively describes the formation of a monolayer of adsorbate on the adsorbent surface, beyond which no further adsorption occurs. In contrast, the Freundlich isotherm describes adsorption on a heterogeneous surface [14]. The equations for the Langmuir and Freundlich isotherms are presented in Eq. (2) and (3), respectively:

$$q_e = \frac{q_m b C_e}{1 + bC_e} \tag{2}$$

$$q_e = K_f C_e^{1/n} \tag{3}$$

where b is a constant related to the free energy of adsorption; q_m is the maximum adsorption capacity (mol g^{-1}); K_f is the Freundlich isotherm constant; and n is the adsorption intensity. For kinetic studies, the pseudo-first-order and pseudo-second-order kinetic models describe the adsorption processes [15]. The equations for these two kinetic models are shown in Eq. (4) and (5):

$$\ln\frac{q_e}{q_e - q_t} = \beta t \tag{4}$$

$$\frac{t}{q_t} = \frac{k}{k_2 q_e^2} + \frac{1}{q_e}t \tag{5}$$

where q_t and q_e are the amounts of adsorbate adsorbed at a given time, t, and at equilibrium, respectively; β and k_2 are the rate constants for the pseudo-first-order and pseudo-second-order kinetic models, respectively.

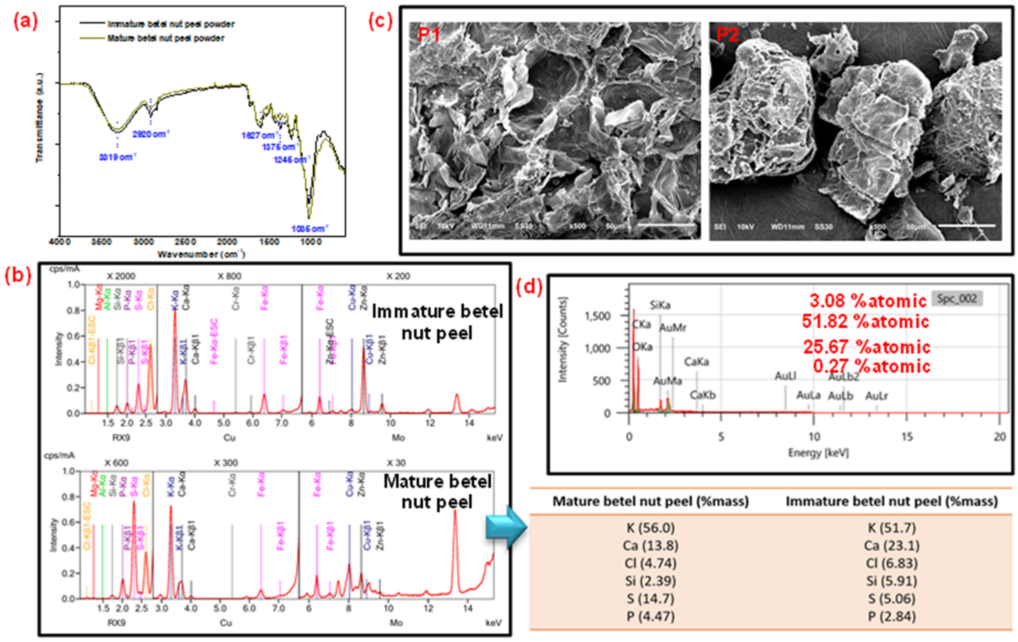
Effectiveness test of biosorbent for adsorbing metal ions in agricultural water

Water samples used as controls were filtered and analyzed for their initial metal content. Subsequently, adsorption was carried out under optimal conditions, and the remaining metal ion content in the solution was analyzed using AAS spectrophotometry.

■ RESULTS AND DISCUSSION

Characterization of Immature and Mature Betel Nut Peel Powders

Betel nut peel is a waste material that can be used as a biosorbent due to its high content of porous fibers consisting of cellulose, lignin, hemicellulose, and pectin [16-17]. Before being applied as a biosorbent, the functional groups present in the betel nut peel powder were characterized using ATR-IR. The ATR-IR spectra of P1 and P2 were very similar, as shown in Fig. 2(a). The presence of the O–H group was indicated by the peak at 3319 cm^{-1} [18]. The stretching vibration of the $C–H_{sp3}$ group was shown at 2920 cm^{-1}. The carbonyl (C=O) group was observed at 1627 cm^{-1}. The aromatic C=C bond appeared at 1375 cm^{-1}, while the C–O stretching group was observed at 1245 cm^{-1}. Additionally, a peak at 1035 cm^{-1} indicated the presence of haloalkane (C–X).



Mature betel nut peel (%mass)	Immature betel nut peel (%mass)
K (56.0)	K (51.7)
Ca (13.8)	Ca (23.1)
Cl (4.74)	Cl (6.83)
Si (2.39)	Si (5.91)
S (14.7)	S (5.06)
P (4.47)	P (2.84)

Fig 2. (a) ATR-IR spectra, (b) XRF spectra and elemental composition, (c) SEM images of P1 and P2, and (d) EDX spectrum of P2

These peaks correspond to those of cellulose, which is a major component of betel nut peel [10,19].

XRF spectra revealed the presence of K, Ca, Cl, Si, S, and P, with the mass percentage of each element shown in Fig. 2(b). The elemental content in the two betel nut peel samples, except for the sulfur content, did not differ significantly. The sulfur content in P2 was nearly three times higher than in P1. In addition to sulfur, the content of positively charged elements, such as Ca, can also serve as adsorption sites through the cation exchange process. The presence of Ca is further confirmed by the EDX results shown in Fig. 2(d).

The abundant pore count is essential for using betel nut peel as a biosorbent. Based on the SEM image in Fig. 2(c), the two betel nut peel samples exhibit distinct pore sizes and shapes. At the same magnification (750 times), P2 shows wider, irregular channel-shaped pores, indicating a larger pore surface area. In contrast, P1 has non-channel pores that are much narrower, resulting in a smaller surface area. This difference in pore structure influences the adsorption activity of the betel nut peel biosorbent [20]. The larger the pores of the biosorbent, the more adsorbates can be trapped or bound to its surface, thereby enhancing its adsorption performance and effectiveness [12,16].

Effect of Adsorbent Mass

The dosage or mass of the adsorbent is often related to the number of active functional groups on the surface that will bind the adsorbate. In theory, a larger mass of adsorbent corresponds to more active groups on the surface [21]. Tests were conducted using varying doses of P1 and P2 at 1, 5, 10, 15, 20, and 30 mg to absorb Mg(II), Ca(II), and Fe(III) at a concentration of 20 mg/L for 60 min. Fig. 3 presents the effect of the adsorbent dose on the metal ion adsorption. The experimental data showed a gradual increase in the adsorption capacity for all three metals in the range of 1–5 mg, reaching an optimum at 5 mg for Mg(II), Ca(II), and Fe(III), with adsorption values of 0.104, 0.113, and 0.200 mg, respectively.

Additionally, no significant changes were observed with a larger adsorbent mass (10–30 mg) or the trend plateaued, indicating that the equilibrium point had been reached [21]. A higher amount of adsorbent could decrease the adsorption capacity due to the possibility of adsorbent clumping, which covers the active sites [22]. Furthermore, the optimal dose of P1 for comparing the three metal ions adsorbed on P2 is shown in Table 1, reveals that the amount of metal ions adsorbed using P2 are higher than those using P1 because the cellulose fibers in P2 contain open pores, making it easier for the adsorbate to be absorbed into the adsorbent's pores.

Kinetics Studies

Kinetic studies help describe the adsorption mechanism by determining the adsorption rate during heavy metal removal, which is evaluated through a mathematical equation [8]. The commonly used kinetic equations for solid and liquid adsorption processes are the pseudo-first-order (Lagergren) and pseudo-second-order (Ho and McKay) models [23]. The optimal contact time provides a removal rate that gradually increases until a steady-state condition is reached [10]. At the equilibrium point, further increases in contact time do not affect the adsorption, and no additional processes occur. Fig. 4 clearly shows that the adsorption of Mg(II), Fe(III), and Ca(II) on P2 occurs faster than on P1. Although both P1 and P2 contain the same O–H group, P2 provides many hollow pores in the cell walls, making it easier to adsorb metal ions [24].

Fig. 4 shows a significant increase in the number of metal ions as the interaction time increases. After reaching the equilibrium point, the concentration of remaining metal ions stabilizes. For P2, the number of metal ions increased gradually and reached an optimum at 60 min, whereas adsorption on P1 progressed more slowly and took up to 90 min. The difference in the contact time is attributed to the distribution of active groups on P2, which reaches equilibrium more quickly than P1. This is because the active O–H groups are more evenly distributed across the surface of the adsorbent, as indicated by the ATR-IR analysis results (Fig. 2(a)).

The data were obtained from the experimental results using pseudo-first-order and pseudo-second-order kinetic equations. Table 2 shows that the k value for P2 is higher than that for P1. The higher rate constant of P2 may be attributed to the presence of fibers in P2, which expand the surface area of the adsorbent through pore diffusion, thereby accelerating the adsorption rate [25].

Isotherm Adsorption

The adsorption isotherm describes the amount of adsorbate remaining in solution (q_e) concerning the concentration in the solution at equilibrium (C_e) [11].

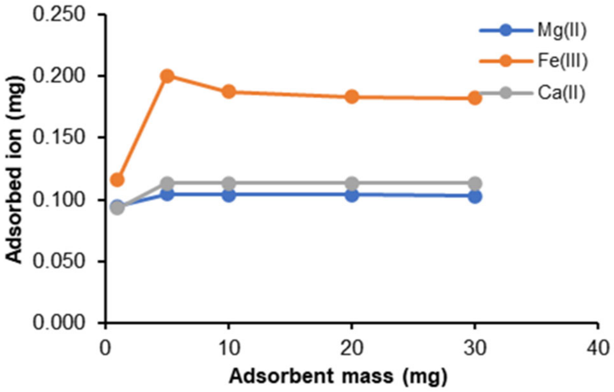


Fig 3. Adsorption of Mg(II), Ca(II), and Fe(III) on P1 at various adsorbent mass

Table 1. Adsorption of metal ions on P1 and P2

Adsorbent	Adsorbed ion (mg)		
	Mg(II)	Ca(II)	Fe(III)
P1	0.104	0.113	0.200
P2	0.248	0.152	0.377

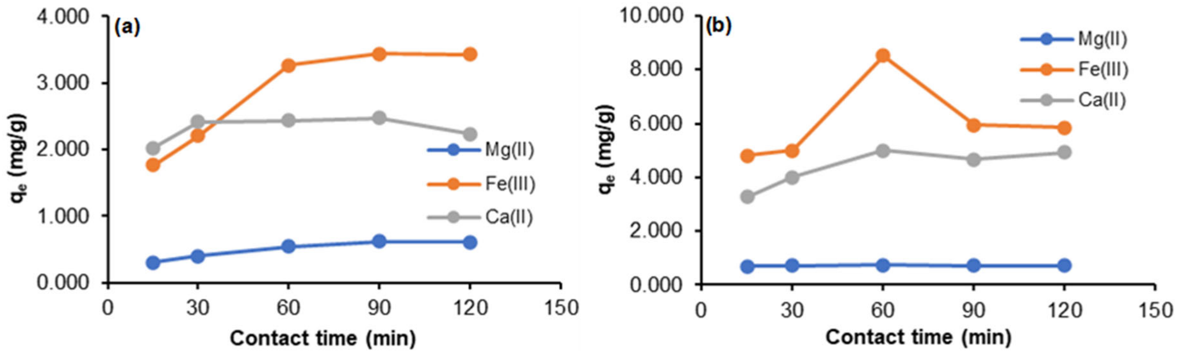


Fig 4. Effect of contact time on the Mg(II), Ca(II), Fe(III) adsorption by (a) P1 and (b) P2

Table 2. Pseudo-second-order parameters of metal ions adsorption on P1 and P2

Metal	P1			P2		
	k_2 (g/mg min^{-1})	q_e (mg/g)	R^2	k_2 (g/mg min^{-1})	q_e (mg/g)	R^2
Mg(II)	0.0616	0.7357	0.9913	3.1732	0.7312	0.9998
Fe(III)	0.0116	4.1271	0.9902	0.0472	6.1463	0.9921
Ca(II)	0.0401	2.2983	0.9914	2.3151	5.2604	0.9948

Isotherms are crucial in interpreting the adsorption process [8]. Isotherm models are commonly used to describe the adsorption of metal ions by biosorbent materials at a specific temperature, such as the Langmuir and Freundlich isotherms. In this study, the adsorption isotherms of Mg(II), Ca(II), and Fe(III) on two types of adsorbents, P1 and P2, were examined by interacting adsorbate solutions at concentrations of 20, 40, 60, 80, 100, and 120 mg/L at the optimum dose and contact time, as shown in Fig. 5. At a constant temperature, both adsorbents exhibit the same pattern: the number of cations adsorbed increases with higher initial adsorbate concentrations until equilibrium is reached at 80 ppm for P1 and 100 ppm for P2. At equilibrium, further additions of metal ions do not cause significant changes [26]. In the adsorption using P2 (Fig. 5(b)), it can be observed that the adsorption of the three metal ions reached optimum conditions at 100 mg/L, with the adsorption capacity of Fe(III) increasing twofold compared to adsorbent P1. This indicates that P2 has more active sites and higher pore availability, which can be occupied by Fe(III) ions [14].

The experimental data were analyzed using the Langmuir and Freundlich isotherm models, and the obtained parameters are presented in Table 3. Based on the correlation coefficient (R^2) being close to 1, the Langmuir isotherm is more suitable for describing the adsorption process of both adsorbents. The Langmuir model assumes that the functional groups on the adsorbent surface are homogeneous, forming a single layer (monolayer) of adsorbate [27]. In other words, all adsorbent sites have an equal chance of being occupied by metal ions [8]. According to the Langmuir model, the maximum adsorption capacity (q_m) of Mg(II), Ca(II), and Fe(III) increased by approximately 1.5 times with P2 adsorbent, with values of 9.61, 19.05, and 45.66 mg/g, respectively. In addition to the increase in q_m, adsorption using P2 provided 2–3 times greater adsorption strength, as seen from the Langmuir equilibrium constant (K_L), compared to P1. In comparison (Table 4), betel nut peel powder shows excellent potential as a natural biosorbent, proving to be much more effective than previously studied biosorbents.

SEM analysis was conducted to observe the structure and morphology of the biosorbent after the adsorption process. EDX analysis was used to determine the semiquantitative composition of metal ions on the biosorbent surface. Compared to the initial biosorbent morphology shown in Fig. 2(c), the structure of the biosorbent underwent noticeable changes with distinct

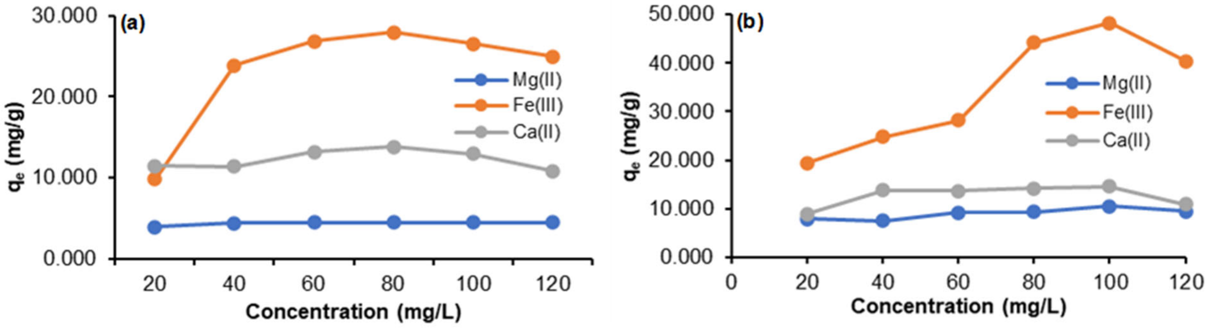


Fig 5. Adsorption of Fe(III), Mg(II), and Ca(II) on (a) P1 and (b) P2 at various initial concentrations

Table 3. Langmuir and Freundlich adsorption isotherm parameters of metal ions on P1 and P2

Adsorbent	Parameters	Ion metal		
		Mg(II)	Fe(III)	Ca(II)
P1	Langmuir			
	q_m (mg g^{-1})	4.51	26.25	14.03
	K_L (L mg^{-1})	25.51	1.76	9.38
	R^2	0.99	0.99	0.99
	Freundlich			
	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	4.07	10.24	12.55
	R^2	0.96	0.91	0.63
	n_F	5.01	3.73	7.17
P2	Langmuir			
	q_m (mg g^{-1})	9.61	45.66	19.05
	K_L (L mg^{-1})	86.75	5.09	2.59
	R^2	0.99	0.99	0.99
	Freundlich			
	K_F (mg g^{-1}) (L mg^{-1})$^{1/n}$	10.31	35.03	13.65
	R^2	0.50	0.16	0.49
	n_F	8.95	9.03	2.65

Table 4. Biosorbents and their maximum adsorption capacity on Fe(III) reported in previous research

Biosorbent	q_m (mg g^{-1})	Ref.
Betel nut skin-activated carbon	1.417	[4]
Carrot	24.330	[28]
Bombax ceiba fruit shell	37.160	[29]
Activated carbon - cherry kernel shell	10.150	[30]
Activated carbon based on rice husk	28.900	[31]
Palmyra palm fruit fibers	0.4147	[32]
Immature betel nut peel powder (P1)	26.250	This study
Mature betel nut peel powder (P2)	45.660	This study

patterns after being used to adsorb specific metal ions. The electronic characteristics and size of the adsorbed metal ion cations likely influence these changes. SEM images and EDX spectra for each biosorbent sample are shown in Fig. 6(a) and 6(b).

Biosorption of Groundwater and Agricultural Water for the Removal of Metal Ion Pollutants

The sorption effectiveness of groundwater (W1) and agricultural water (W2) using mature betel nut peel was assessed through organoleptic tests, including odor and color parameters. Additionally, a pH meter and AAS spectrophotometry measured the quality and percentage of metal content removal from W1 and W2 samples before and after treatment. Both water samples exhibited an unpleasant odor based on the physical parameter values before adsorption. This condition is likely caused by dissolved organic compounds in the water, resulting from the decomposition process of microorganisms, chemical compounds, and heavy metals in the aquatic environment [7,33]. Research by Selmi et al. [9] noted an increase in the pH of sample W1 from 5 to 6.5 (close to neutral), attributed to the interaction between functional groups on the adsorbent and contaminants in the water. The acidity was influenced by the presence of fulvic and humic acids, which are types of aromatic carbon compounds that are difficult to decompose in water and flow into the infiltration well water [34].

From Table 5, it can be observed that the concentration of Fe exceeds the required quality standard

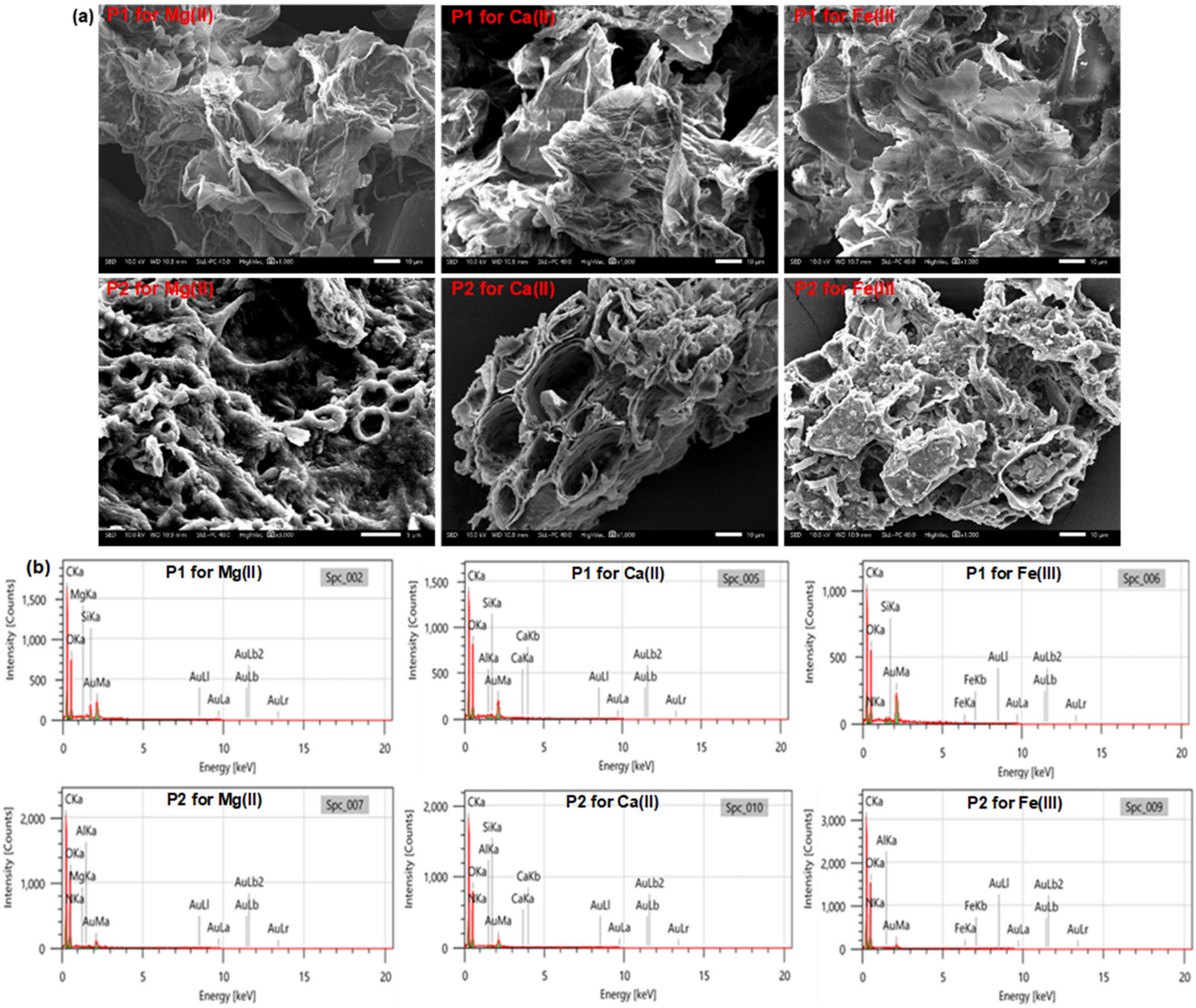


Fig 6. (a) SEM images and (b) EDX spectra of biosorbents after adsorption

Table 5. Parameter of the physicochemical factor of both W1 and W2 using P2

Parameters		Groundwater (W1)		Agricultural		Standard*
		Initial	After adsorption	Initial	After adsorption	
Physics	Odor	Slight smell	Stink, strong odor	No odor	Slight smell	No odor
	Color	Slight muddy	Deep yellow, muddy	Clear	Yellowish	No color
Chemical	pH	5.00	6.50	7.50	7.50	6.5–9.0
	Mg(II) (mg L^{-1})	15.74	1.12	38.43	13.20	500 mg L^{-1}
	Ca(II) (mg L^{-1})	19.04	1.53	39.54	9.52	
	Fe(III) (mg L^{-1})	16.56	1.58	19.69	1.66	1.0 mg L^{-1}

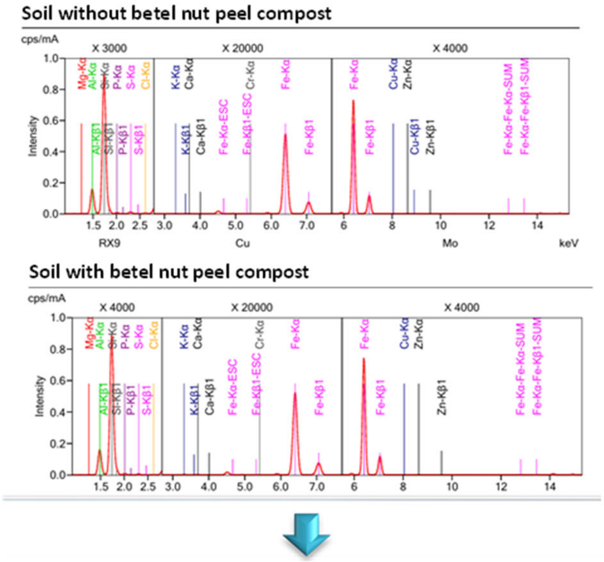
*Regulation of the Minister of Health Republic of Indonesia Number 416/MENKES/PER/IX/1990

of 1.0 mg/L. The significant presence of Fe in the water is primarily due to leaching processes, fertilizers, runoff from industrial activities, and irrigation of crop fields, all of which contribute to the contamination of the aquatic environment [7]. Conditions before adsorption in well water and agricultural water are influenced by the sampling point's location, which is near an industry that heavily utilizes iron in its activities. For instance, the use of rusted pipes can increase the Fe content in the water [35-36].

Fe ions can decompose in water and enter water bodies through ditches or rainwater runoff from the soil. Additionally, high levels of Fe ions, which serve as a micronutrient, can inhibit the fixation of other elements. Fe(III) ions are typically present as ferrous cations (Fe^{2+}) in aqueous solutions, while ferric cations (Fe^{3+}) easily precipitate in water with a pH of around 7 and sufficient dissolved oxygen levels. Based on XRF analysis (Fig. 7), soil samples taken from farms showed that agricultural soil not treated with betel nut peel compost had lower iron content compared to soil samples that were treated. This highlights the importance of applying biosorbent to betel nut peel powder in agricultural water. According to the government regulation of the Republic of Indonesia No. 82 of 2001, classes II, III, and IV for agricultural water should have an iron content of no more than 20 mg/L. As a comparison, the adsorption efficiency for removing Mg(II), Fe(III), and Ca(II) metals using both P1 and P2 is observed in Table 6. After the adsorption process, the Fe(III) ions approach the quality standards set by the Indonesian Ministry of Health, with the percentage of Fe metal removal using P2 in W1 and W2 reaching 90%. Based on previous studies shown in Table 4, it is evident that the adsorption capacity of the tested betel nut peel biosorbent is significantly superior to that of earlier adsorbents. Although highly efficient and selective in attracting Fe(III) metal ions, this biosorbent would benefit from modification with magnetic materials to facilitate the separation process.

Adsorption of Mg(II), Ca(II), and Fe(III) on Betel Nut Peel Powders

Adsorption is a separation process in which specific components from the liquid phase are attracted



Soil Without Betel Nut Peel Compost (% mass)	Soil With Betel Nut Peel Compost (% mass)
Si (55.30)	Si (58.30)
Fe (23.90)	Fe (19.70)
Al (17.80)	Al (18.40)
K (1.240)	K (1.720)
Ca (0.775)	Ca (0.893)
Mg (0.369)	Mg (0.408)
P (0.280)	P (0.352)
S (0.236)	S (0.138)
Zn (0.056)	Zn (0.044)
Cl (0.050)	Cl (0.037)
Cu (0.018)	Cu (0.016)
Cr (0.006)	Cr (0.003)

Fig 7. XRF spectra of agricultural soil samples and their element composition

Table 6. Adsorption efficiency of three metal ions on betel nut peel biosorbents

Adsorbent/water sample	Metal ion contents (mg L^{-1})						Percentage removal efficiency (%)		
	Initial sample			After adsorption					
	Mg(II)	Fe(III)	Ca(II)	Mg(II)	Fe(III)	Ca(II)	Mg	Fe	Ca
P1/W1	15.74	16.56	19.04	2.76	1.66	1.57	82.45	90.00	91.76
P2/W1	15.74	16.56	19.04	1.12	1.58	1.53	92.87	90.47	91.98
P1/W2	38.43	19.70	39.54	12.28	2.44	16.95	68.04	87.62	57.14
P2/W2	38.43	19.70	39.54	13.20	1.65	9.52	65.65	91.59	75.93

to the surface of a solid adsorbent. This process involves the movement of the adsorbate's ions, atoms, or molecules, which attach to the adsorbent's surface, forming bonds through physical forces or chemical interactions, thereby transferring components from the liquid phase. In this study, several metal ion adsorption mechanisms are involved when using betel nut peel biosorbents (Fig. 8). Physical adsorption occurs through van der Waals forces, hydrogen bonds, polarity, and dipole-dipole interactions. Second, chemical adsorption (chemisorption) involves the formation of strong bonds between the adsorbate and the adsorbent, often facilitated by specific functional groups on the surface of the adsorbent through ion exchange or complexation. Biomass-based adsorbents, like betel nut peel biosorbents, offer a promising solution for removing hazardous pollutants from industrial and agrochemical activities. XRF data from Fig. 2(b) indicates that the sulfur content in P2 is nearly 3 times higher than in P1. The negative charge of sulfur enables the absorption of metal ions through electrostatic interactions, where the positively charged metal ions from the solution interact with the negatively charged groups on the biomass cell wall. The pH$_{pzc}$ value helps determine the electrostatic interactions between cations and anions. The pH$_{pzc}$ is defined as the pH at which the adsorbent surface has no net charge, with betel nut peel reported to have a pH$_{pzc}$ value of 3.7 [36]. At a pH higher than the pH$_{pzc}$, the active sites of the adsorbent will carry a negative charge [37-38]. This is consistent with the pH values observed after adsorption in groundwater (6.5) and agricultural water (7.5), as shown in Table 5.

■ CONCLUSION

A batch adsorption study of Mg(II), Ca(II), and Fe(III) ions on betel nut peel biosorbent was conducted, evaluating the effects of initial adsorbate concentration, biosorbent dosage, and adsorption time. The adsorption kinetics for both P1 and P2 adsorbents followed a pseudo-second-order model, while the Langmuir model best represented the isotherm data. The adsorption capacities

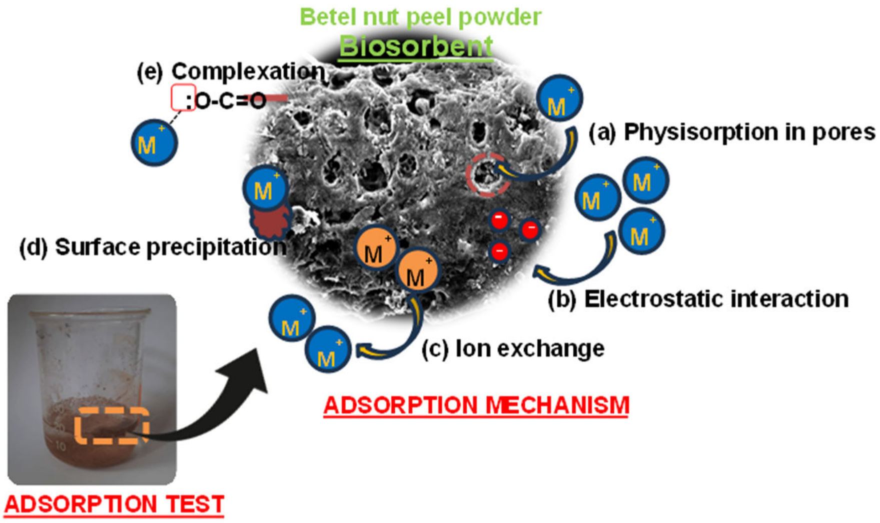


Fig 8. Several possible adsorption mechanisms occur in betel nut peel powder

for Mg(II), Ca(II), and Fe(III) ions were 9.61, 19.05, and 45.66 mg g^{-1}, respectively. The results demonstrated that biosorbent derived from mature betel nut peel effectively adsorbed Mg(II), Ca(II), and Fe(III) ions in groundwater and agricultural water samples. The P2 biosorbent use in groundwater and agricultural water significantly reduced Fe(III) concentrations by up to 90%, showing promise for further development as a sustainable, renewable material for adsorption and biofertilizer applications.

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■ CONFLICT OF INTEREST

All authors declare that they have no conflict of interest.

■ AUTHOR CONTRIBUTIONS

Carissa Ayu Susiana conducted the experiment, wrote the original draft, and performed the calculations. Feri Mukhayani was responsible for the visualization, wrote the original draft, and revised and edited the manuscript. Nuryono handled the conceptualization, methodology, supervision, funding acquisition, and review and editing of the draft. Fajar Inggit Pambudi contributed to the methodology, validation, project administration, review, and editing. I Wayan Sumerta, Erwinton Simatupang, Guntur Mulyanegara, Mohammad Nur Samudin, and Dedo Kevin Prayoga contributed to the methodology, project administration, and validation. All authors on this project have agreed to the final version of the manuscript.

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