# scientific reports



## **The high adsorption performance OPEN of banana (***Musa* **ABB Cv. Kluai 'Namwa') beaded materials modified with zinc and magnesium oxides for cadmium removal**

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**Wastewater contaminated with cadmium is a concern because of its toxicity, persistence, and bioaccumulation to the environment, ecosystem, and human health, so it is required to remove cadmium(II) ions before releasing them to receiving water. Banana powder beads (BPB), banana powder doped ZnO beads (BPZB), banana powder doped MgO beads (BPMB), and banana powder doped ZnO+MgO beads (BPZMB) were synthesized as the novel cadmium adsorbents, and their characterizations, cadmium adsorption performances, cadmium adsorption patterns and mechanisms, thermodynamic study, and reusability were investigated. BPMB had the highest specific surface area of 16.60 m2/g and the smallest pore size of 1.69 nm than other materials. BPB was an amorphous structure, whereas BPZB, BPMB, and BPZMB were crystalline structures presenting their specific metal oxide peaks of ZnO or MgO. They were coarse surfaces and had a spherical shape consisting of C, O, Ca, Cl, and Na. Their main functional groups were O–H, C–H, C=O, C–O, and N–H. The points of zero charge of BPB, BPZB, BPMB, and BPZMB were 5.37, 6.75, 9.87, and 9.43. The cadmium removal efficiencies of BPB, BPZB, BPMB, and BPZMB were 89.18%, 96.62%, 99.59%, and 97.85%, and their**  $q_m$  **values were 90.09, 232.56, 454.55, and 303.03 mg/g, respectively. Thus, the metal oxide helped to improve material efficiency, especially MgO. The Freundlich and pseudo-second-order kinetic models were good fit models for describing their adsorption patterns and mechanisms. The increasing temperature affected to decrease their cadmium adsorptions. They could be reused in more than 3 cycles of more than 73% of cadmium adsorption. The electrostatic interaction played an important role in describing their cadmium adsorptions. Therefore, BPBM was a good cadmium adsorbent for application in industrial wastewater treatment since it had a higher performance of cadmium adsorption than other materials.**

**Keywords** Fruit waste, Metal oxide, Adsorption, Heavy metal, Reusability

The toxicities of heavy metals are generally known to affect many human health effects of main function disorders and many human diseases. The high-risk effect depends on the type of heavy metals which mercury, cadmium, and lead are the top three highly dangerous heavy metals with high toxicities causing human carcinogenesis. Many industries of battery, metal plating, steel, dyes, pigments, pharmaceutical products, and ceramics use cadmium in their manufacturing processes, so their wastewater may have cadmium contamination. Thus, they need to be eliminated before releasing to receiving water. The United States Environmental Protection Agency (USEPA) is also required to treat cadmium-contaminated wastewater to be below 0.005 mg/L for drinking water, and the World Health Organization (WHO) is recommended not to exceed 0.03 mg/L in wastewater $^{\rm l}$ .

Many previous studies popularly used the adsorption method for several heavy metal removals more than other methods of chemical precipitation, electrodialysis, ion exchange, membrane separation, photocatalysis, and nanotechnology because it is an effective method, easy operation, low energy requirement, many options of adsorbents, and reasonable operation cost. Many options of adsorbents might be from agriculture, industry,

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and waste for eliminating target pollutants. Among those adsorbents, waste adsorbents are interesting because they can adsorb many heavy metals and save operating costs. Moreover, they are a good way of waste recycling to offer waste-sustainable uses. Many waste adsorbents from industry, agriculture, animal, vegetable, and fruit for heavy metal removals are illustrated in Table [1.](#page-1-0) Among those adsorbents, fruit wastes are interesting because they can adsorb various heavy metals and reduce a large amount of waste from human consumption resulting in good waste management. Especially, banana is a popular human fruit around the world resulting in an abundant amount of banana peels. Since they have good chemical compositions of cellulose, hemicellulose, pectin, and lignin, they are used for eliminating pollutants in wastewater in many previous studies in Table [1.](#page-1-0)

Several methods by thermal, alkaline, acid, and metal oxide modifications have been studied in many previous studies to improve the material efficiency of fruit peels for target heavy metals shown in Table [2](#page-2-0). The thermal method used a temperature from 200 to 550 °C to prepare pomelo, banana, and mango peels to be biochar for adsorbing copper(II) and cadmium(II) ions<sup>2-[4](#page-20-2)</sup>. For the alkaline method, sodium hydroxide (NaOH) was used for activating melon and lemon peels to remove copper(II), cadmium(II), and nickel(II) ions<sup>[5,](#page-20-3)[6](#page-20-4)</sup>. For the acid treatment, phosphoric acid  $(H_3PO_4)$  and hydrochloric acid (HCl) were applied to activate banana peels to adsorb cadmium(II) and chromium(VI) ions<sup>[7,](#page-20-5)[8](#page-20-6)</sup>. For the metal oxide modifications, metal oxides of iron(II, III) oxide (Fe<sub>3</sub>O<sub>4</sub>), titanium dioxide (TiO<sub>2</sub>), aluminum oxide (Al<sub>2</sub>O<sub>3</sub>), and magnesium oxide (MgO) were used to modify pomelo, pomegranate, banana, and watermelon peels for eliminating lead(II), copper(II), arsenic(III), and cadmium(II) ions<sup>[2,](#page-20-1)[9](#page-20-7)[–11](#page-20-8)</sup>. Among those methods, the addition of metal oxide into fruit peels gave a higher adsorption capacity  $(q_m)$  than other methods. As a result, this method is an interesting use to improve material efficiency for heavy metal removals. For banana peels, they were modified by thermal, acid, and aluminum oxide  $(Al_2O_3)$  in a powder form for removing lead(II) ions<sup>[7](#page-20-5)[,12](#page-20-9),13</sup>, and they were also modified by acid and  $Al_2O_3$ in a powder form for adsorbing cadmium(II) and chromium(VI) ions<sup>[7,](#page-20-5)[8](#page-20-6),13</sup>. However, no one used zinc oxide (ZnO) or magnesium oxide (MgO) for modifying banana peels in a bead form to remove cadmium(II) ions in aqueous solution, so it was a research gap to develop a low-cost adsorbent from banana peels as a novel cadmium adsorbent. Therefore, this study was the first attempt to synthesize novel cadmium adsorbents from

<span id="page-1-0"></span>

**Table 1**. Waste adsorbents for eliminating heavy metals.

<span id="page-2-0"></span>

**Table 2**. Acid, alkaline, thermal, and metal oxide modifications in fruit peels for heavy metal removals.

banana peels with or without modification of ZnO or MgO in a bead form to investigate how much ZnO or MgO increases banana material efficiency for cadmium adsorption. Moreover, the addition of one metal oxide (ZnO or MgO) or two metal oxides of ZnO+MgO into banana peel materials should be chosen for obtaining high cadmium adsorption. Furthermore, this study also presented a novel material form of cadmium adsorbents for easy separation after treatment which might be applied in industrial applications to save operation costs as well.

This study aimed to synthesize banana powder beads with ZnO or MgO modifications which were banana powder beads (BPB), banana powder doped ZnO beads (BPZB), banana powder doped MgO beads (BPMB), and banana powder doped ZnO+MgO beads (BPZMB) for cadmium removals in aqueous solution. Their physiochemical properties on specific surface area, pore volumes, and pore size, crystalline structures, surface morphologies, chemical compositions, functional groups, and points of zero charge were also studied by Brunauer-Emmett-Teller (BET), X-ray diffractometer (XRD), Field emission scanning electron microscopy and focus ion beam (FESEM-FIB) with energy dispersive X-ray spectrometer (EDX), and Fourier transform infrared spectroscopy (FT-IR). Moreover, their cadmium removal efficiencies were investigated by a series of batch experiments, adsorption isotherms, and kinetics. The temperature effects on their cadmium removals were also explored by the thermodynamic study, and the desorption experiments were used for studying the material reusability.

### **Materials and methods**

#### **Raw material preparation**

*Musa* ABB cv. Kluai 'Namwa' peels were obtained from a fried banana shop in Khon Kaen province, Thailand. They were washed with tap water to eliminate the contaminants, and then they were dried in a hot air oven (Binder, FED 53, Germany) at 80 °C overnight. After that, they were blended and sieved in size of 125 μm. Finally, they were kept in a desiccator before use called banana powder  $(BP)^{20,30}$  $(BP)^{20,30}$  $(BP)^{20,30}$  $(BP)^{20,30}$ .

#### **Chemicals**

The chemicals used in this study were an analytical grade used without purification, and the details were demonstrated in the supplementary material.

#### **Banana material synthesis**

Banana material synthesis consisted of two steps which were banana powder modifications by zinc oxide (ZnO) or magnesium oxide (MgO) and banana bead materials with or without metal modifications which modified an idea from the studies of Praipipat, P et al.<sup>[31](#page-21-10),30</sup>. The schematic flow diagram of banana material synthesis is demonstrated in Fig. [1](#page-3-0) and the details were clearly described in the supplementary material.

#### **Material characterizations**

The material characterizations of BPB, BPZB, BPMB, and BPZMB were investigated with several characterized equipment, and the details are demonstrated in Table [3.](#page-4-0)

<span id="page-3-0"></span>

**Fig. 1**. The schematic flow diagram of banana material synthesis for banana powder beads (BPB), banana powder doped ZnO beads (BPZB), banana powder doped MgO beads (BPMB), and banana powder doped ZnO+MgO beads (BPZMB).

#### **The points of zero charge**

The points of zero charge  $(pH_{pxc})$  of BPB, BPZB, BPMB, and BPZMB were studied following the method of Praipipat et al.<sup>31</sup> by using 50 mL of 0.1 M NaCl solutions at pH 1-12 and 0.1 g of material with shaking at 150 rpm for 24 h. After that, the final pH solution was measured by a pH meter (Mettler Toledo, Seven2Go pH with InLab Expert Go-ISM, Switzerland) and the graph of ∆pH (pH<sub>final</sub> – pH<sub>initial</sub>) versus pH<sub>initial</sub> was plotted to determine  $pH_{pzc}$ .

<span id="page-4-0"></span>

#### **Table 3**. The details of material characterizations.

<span id="page-4-3"></span>

**Table 4**. Adsorption isotherm and kinetic models.

#### **A series of batch experiments**

The material dosage (0.02–0.5 g), contact time (1–12 h), temperature (20–50 °C), pH (3–10), and initial concentration (25–200 mg/L) of BPB, BPZB, BPMB, and BPZMB were examined by a series of batch experiments. The cadmium concentration of 100 mg/L, 100 mL of sample volume, and shaking speed of 150 rpm were applied as the control condition, and the triplicate samples were used to confirm the results. The optimum condition was chosen from the lowest value of each affecting factor obtaining the highest cadmium removal efficiency, and it was used for the next affecting factor. The atomic absorption spectrophotometry (AAS) (PerkinElmer, PinAAcle 900 F, USA) was used to measure the cadmium concentration. Cadmium removal efficiency (%) and the cadmium adsorption capacity  $(q_e)$  (mg/g) were calculated by Eqs. ([1](#page-4-1)) and ([2](#page-4-2)), respectively.

$$
Cadmium removal efficiency (\% ) = (C_0 - C_e)/C_0 \times 100 \tag{1}
$$

<span id="page-4-2"></span><span id="page-4-1"></span>where  $C_0$  is the initial cadmium concentration (mg/L), and  $C_e$  is the final cadmium concentration (mg/L).

The cadmium adsorption capacity 
$$
(q_e) = ((C_0 - C_e) \times V/M)
$$
 (2)

where *V* is the sample volume (L), and *M* is the mass of material (g).

#### **Adsorption isotherms and kinetics**

The details of adsorption isotherm and kinetic models used in this study to determine the adsorption patterns or mechanisms of BPB, BPZB, BPMB, and BPZMB are illustrated in Table [4.](#page-4-3)

For the adsorption isotherms, 0.2 g of BPB or 0.08 g of BPZB or 0.04 g of BPMB, or 0.06 g of BPZMB was added into 250 mL of Erlenmeyer flask containing 100 mL of different cadmium concentrations from 25 to 200 mg/L, pH 5, and tested the cadmium adsorption by an incubator shaker (New Brunswick, Innova 42, United State) at 25 °C for BPZB and BPMB or 35 °C for BPB and BPZMB with a shaking speed of 150 rpm at 5 h for BPZB, BPMB, and BPZMB or 8 h for BPB.

For the adsorption kinetics, 2 g of BPB or 0.8 g of BPZB or 0.4 g of BPMB, or 0.6 g of BPZMB was added into 1000 mL of breaker containing 1000 mL of 100 mg/L of cadmium concentration, pH 5, and tested the cadmium adsorption by a jar test (JAR-TESTER, SF6, South Korea) with a shaking speed of 150 rpm for 12 h.

#### **Thermodynamic study**

<span id="page-5-0"></span>Thermodynamic study was used to explore the temperature effect from 293.15 to 323.15 K on the cadmium removal efficiency of BPB, BPZB, BPMB, and BPZMB. The Eqs. [\(3](#page-5-0))-([5](#page-5-1)) were used for calculating the thermodynamic parameters<sup>[40](#page-21-19)</sup>.

$$
\Delta G^o = -RT \ln K_c \tag{3}
$$

<span id="page-5-1"></span>where *R* is the universal gas constant (8.314 J/mol K), *T* is the absolute temperature (K), and  $K_c$  is the equilibrium constant (L/mg).

$$
\ln K_c = -\Delta H^o / RT + \Delta S^o / R \tag{4}
$$

$$
\Delta G^o = \Delta H^o - T\Delta S^o \tag{5}
$$

where Δ*H*<sup>°</sup> and Δ*S*<sup>°</sup> values are calculated from the slope and intercept of the linear graph between ln *K*<sub>c</sub> (*K*<sub>c</sub> =  $q_e/C_e$ ) and 1/*T*.

For the thermodynamic study, 0.2 g of BPB or 0.08 g of BPZB or 0.04 g of BPMB or 0.06 g of BPZMB was added to 250 mL of Erlenmeyer flask containing 100 mL of 100 mg/L cadmium concentration, pH 5, and tested the cadmium adsorption by an incubator shaker with different temperatures from 293.15 to 323.15 K with a shaking speed of 150 rpm at 5 h for BPZB, BPMB, and BPZMB or 8 h for BPB.

#### **Material reusability**

<span id="page-5-2"></span>Material reusability of BPB, BPZB, BPMB, and BPZMB was examined by the desorption experiment following the method of Praipipat et al.<sup>14</sup> by using  $0.5 M HNO<sub>3</sub>$  pushed out cadmium(II) ions from the saturated material with shaking at 150 rpm for 6 h, rinsed with deionized water, and air-dried before use in the next adsorption cycle. The cadmium desorption efficiency (%) is calculated by Eq. [\(6\)](#page-5-2).

\n
$$
\text{Cadmium} \quad \text{desorption} \quad \text{efficiency} \quad (\% \quad) = (q_d/q_a) \times 100
$$
\n

where  $q_{\rm d}$  is the amount of cadmium desorbed (mg/L) and  $q_{\rm a}$  is the amount of cadmium adsorbed (mg/L).

#### **Result and discussion**

#### **The visual appearances of materials**

The visual appearances of BPB, BPZB, BPMB, and BPZMB are shown in Fig. [2a](#page-6-0)-d which had a spherical shape with different colors with approximately 1 mm in size. BPB were black color beads, whereas BPZB were dark brown color beads. For BPMB and BPZMB, they were light brown color beads. Therefore, metal oxides of zinc and magnesium resulted in a change in the material color of banana beads.

#### **Material characterizations**

*BET*

The physicochemical properties on the specific surface area, pore volumes, and pore sizes of BPB, BPZB, BPMB, and BPZMB were determined by BET analysis and reported by the Barrett-Joyner-Halenda (BJH) adsorption method demonstrated in Table [5.](#page-6-1)

For the specific surface area, BPMB had a higher specific surface area of  $16.60 \text{ m}^2/\text{g}$  than other materials, so the addition of MgO affected the increase of the specific surface area of banana peel materials more than ZnO similar reported by the previous studies used MgO and ZnO to modify sugarcane bagasse and bagasse fly ash for adsorbing direct red 28 dye<sup>[41,](#page-21-20)[42](#page-21-21)</sup>. In addition, the pore volume results corresponded to the specific surface area that BPMB had the highest pore volume of 0.0388 cm<sup>3</sup>/g. The pore size of BPMB was 1.69 nm which was smaller than other materials. Following the International Union of Pure and Applied Chemistry(IUPAC) classification, the sizes of material are classified as microporous size ( $\lt 2$  nm) and mesoporous size ( $2-50$  nm)<sup>24</sup>. Thus, BPB and BPZB were mesoporous materials, whereas BPMB and BPZMB were microporous materials. Since BPMB had the highest specific surface area and smallest pore size, it might have the ability to adsorb cadmium ions than other materials.

#### *XRD*

The crystalline structures of BPB, BPZB, BPMB, and BPZMB by XRD analysis are demonstrated in Fig. [3](#page-7-0)a-d. BPB was the amorphous structure shown in Fig. [3](#page-7-0)a whereas other materials displayed the crystal structures with presenting their metal oxide specifically peaks illustrated in Fig. [3](#page-7-0)b-d. For BPZB, it had the specific peaks of ZnO at the positions of 100, 002, 101, 102, 110, 103, 200, 112, 201, 004, and 202 (JCPDS no.36-1451) presented in Fig. [3b](#page-7-0) similar detected by previous studies used ZnO to modify bagasse, bagasse fly ash, chicken and duck eggshells for adsorbing reactive blue 4 dye<sup>[43,](#page-21-22)[44](#page-21-23)</sup>. For BPMB, it presented the specific peaks of MgO at the positions of 220, 111, 200, and 220 (JCPDS no.65–0476) demonstrated in Fig. [3](#page-7-0)c similar observed by a previous study that used MgO to load into biochar for removing lead(II) and cadmium(II) ions<sup>45</sup>. For BPZMB, it displayed the specific peaks of ZnO at the same positions with BPZB and MgO at the positions of 220, 111, and 220 which the

<span id="page-6-0"></span>

**Fig. 2**. The visual appearances of (a) BPB, (b) BPZB, (C) BPMB, and (d) BPZMB.

<span id="page-6-1"></span>

**Table 5**. The physiochemical properties on specific surface area, pore volumes, and pore sizes of BPB, BPZB, BPMB, and BPZMB.

ZnO dominated in BPZMB with higher intensity than MgO shown in Fig. [3](#page-7-0)d. Therefore, the results of the XRD analysis confirmed the successful addition of ZnO or MgO into banana peel materials.

#### *FESEM-FIB and EDX*

The surface morphologies of BPB, BPZB, BPMB, and BPZMB were analyzed by FESEM-FIB analysis, and the results are illustrated in Fig. [4](#page-8-0)a-h. For Fig. [4a](#page-8-0)-d, they demonstrated the beaded materials at the magnification of 100X with 1 mm which were coarse surfaces with having a spherical shape. For Fig. [4](#page-8-0)e-h, they displayed their surface morphologies by a cross-section at the magnification of 1,500X with 100 μm which were coarse and heterogeneous surfaces.

The chemical compositions of BPB, BPZB, BPMB, and BPZMB were analyzed by EDX analysis, and the results are illustrated in Table [6](#page-8-1) reported in the percentage by weight (%wt). Carbon (C), oxygen (O), calcium (Ca), chlorine (Cl), and sodium (Na) were observed in BPB, BPZB, BPMB, and BPZMB which are generally

<span id="page-7-0"></span>

**Fig. 3**. The crystalline structures of (a) BPB, (b) BPZB, (C) BPMB, and (d) BPZMB.

found in fruit peels similar observed by previous studies<sup>[31](#page-21-10),46</sup>. In addition, Na, Ca, and Cl might form the chemicals of sodium alginate ( $\text{NaC}_6\text{H}_2\text{O}_6$ ) and calcium chloride dihydrate (CaCl<sub>2</sub>.H<sub>2</sub>O) used for synthesizing bead materials. Furthermore, BPZB, BPMB, and BPZMB also detected zinc (Zn) or magnesium (Mg). The elemental distributions of BPZB, BPMB, and BPZMB shown in Fig. [4](#page-8-0)i-l could confirm the addition of ZnO or MgO into banana peel materials and found Zn or Mg distributions in BPZB, BPMB, and BPZMB.

<span id="page-8-0"></span>

**Fig. 4**. The surface morphologies of (a and e) BPB, (b and f) BPZB, (c and g) BPMB, and (d and h) BPZMB, and the elemental distributions of(I) BPZB, (j) BPMB, and (k and l) BPZMB.

<span id="page-8-1"></span>

**Table 6**. The chemical elements of BPB, BPZB, BPMB, and BPZMB.

#### *FT-IR*

The main chemical functional groups of BPB, BPZB, BPMB, and BPZMB identified by FT-IR analysis were O–H, C–H, C=O, C–O, and N–H. Moreover, the specific functional group of metal oxide with oxygen bond (Zn–O or Mg–O) was detected in BPZB or BPMB, or BPZMB found in a range of 600 cm<sup>−</sup>1[42](#page-21-21). The results are demonstrated in Fig. [5](#page-9-0)a-d. For O–H, it represented the hydroxyl group with the stretching or bending vibrations observed in the ranges of 3200 and 1400 cm<sup>-1</sup> generally found on pectin, cellulose, hemicellulose, and lignin in banana peels<sup>47</sup>. In addition, it presented the hydroxyl group with the stretching vibration in MgO

<span id="page-9-0"></span>

**Fig. 5**. FT-IR spectra of (a) BPB, (b) BPZB, (c) BPMB, and (d) BPZMB.

at 3600 cm−<sup>1</sup> similar detected by previous studies that used MgO for modifying sugarcane bagasse and bagasse fly ash[41](#page-21-20),[42](#page-21-21)[,48](#page-21-27). For C–H, it was C–H stretching vibration in cellulose presenting in a range of 2800–2900 cm−<sup>1</sup> found in banana peel[s49](#page-21-28). Moreover, the C–H stretching vibration in alkenes and aromatics was detected in a range of 700 cm<sup>−1</sup> similar observed by the study of Akter, et al. used banana peels for removing dyes from textile effluent<sup>50</sup>. For C=O, it presented the carboxyl stretching vibration in carbohydrates and lignin found in a range of 1500–1600 cm<sup>−</sup>[150](#page-21-29). For C–O, it represented the carbonyl stretching vibrations of C–O–C of sodium alginate and cellulose at approximately 1020 cm<sup>−1</sup> agreed with a previous study that used sodium alginate for synthesizing beaded materials from fruit peels<sup>46</sup>. In addition, it also referred to C–O of ester and ether in a range of 870–890 cm<sup>−</sup>[150](#page-21-29). For N–H, it was the deformation of amines at approximately 816 cm−[149](#page-21-28).

#### *The points of zero charge*

The points of zero charge ( $pH_{pzc}$ ) of BPB, BPZB, BPMB, and BPZMB were 5.37, 6.75, 9.87, and 9.43, respectively demonstrated in Fig. [6](#page-10-0) which BPMB had a higher pH<sub>pzc</sub> than other materials. Thus, the additions of MgO or ZnO increased the pH<sub>pzc</sub> of materials, especially MgO similar found in previous studies that used MgO and ZnO for modifying sugarcane bagasse and bagasse fly ash for removing direct red 28 dye<sup>[41,](#page-21-20)[42](#page-21-21)</sup>. Moreover, the pH<sub>pzc</sub>

<span id="page-10-0"></span>

**Fig. 6**. The points of zero charge of BPB, BPZB, BPMB, and BPZMB.

values of BPMB and BPZMB were in an alkaline range similar to other studies reporting the  $\rm pH_{pzc}$  of materials with adding MgO to be found in an alkaline range  $42,48$  $42,48$ .

#### **A series of batch experiments**

Cadmium removal efficiencies by BPB, BPZB, BPMB, and BPZMB were investigated by a series of batch experiments. The results are demonstrated in Fig. [7](#page-11-0)a-f.

<span id="page-11-0"></span>

**Fig. 7**. Cadmium adsorptions by a series of batch experiments on the effects of (a and b) dose, (c) contact time (d) temperature, (e) pH, and (f) initial concentration of BPB, BPZB, BPMB, and BPZMB.

For the effect dose, the increase of material dosage resulted in the increase of cadmium removal efficiencies of BPB, BPZB, BPMB, and BPZMB from 0.02 to 0.2 g for BPB and from 0.02 to 0.08 g for BPZB, BPMB, and BPZMB, and then they were constant shown in Fig. [7](#page-11-0)a and b. The increase of material dosage increased the active site of material to capture cadmium(II) ions similar reported by the study of Ramutshatsha-Makhwedzha, et al. used activated carbon banana peels coated  $\text{Al}_2\text{O}_3$ -chitosan for removing lead and cadmium from wastewater<sup>[13](#page-20-10)</sup>. The constant cadmium removal efficiency meant it went into the equilibrium of cadmium adsorption similar found by a previous study[13.](#page-20-10) Moreover, the highest cadmium removal efficiencies of BPB, BPZB, BPMB, and BPZMB were found at 0.2 g for 85.50%, 0.08 g for 100%, 0.04 g for 100%, and 0.06 g for 100%, respectively, and they were used as the optimum material dosages in the contact time effect. Therefore, the addition of ZnO or MgO increased material efficiency by spending less adsorbent dosage than material without modification.

For the contact time effect, the cadmium removal efficiency of BPB was increased with increasing contact time from 1 to 8 h, whereas the cadmium removal efficiencies of BPZB, BPMB, and BPZMB were increased with increasing contact time from 1 to 5 h. The increase in contact time results in the increase of adsorption time between adsorbate on adsorbent. After that, they were constant which represented the saturated adsorption on adsorbent<sup>20</sup>. The results are demonstrated in Fig. [7](#page-11-0)c. The highest cadmium removal efficiency of BPB was found at 8 h for 89.54%, whereas the highest cadmium removal efficiencies of BPZB, BPMB, and BPZMB were found at 5 h at 96.69%, 100%, and 98.65%, respectively. The optimum material dosage and contact time of each material were applied to study the temperature effect. Therefore, the metal modifications by ZnO or MgO increased material efficiency by decreasing the adsorbent dosage and contact time for cadmium adsorption.

For temperature effect, the results are illustrated in Fig. [7](#page-11-0)d. The highest cadmium removal efficiencies of BPB and BPZMB were found at 35 °C for 87.63% and 95.85%, whereas the highest cadmium removal efficiencies of BPZB and BPMB were found at 25 °C for 93.81% and 99.53%. As a result, a temperature of 35 °C was chosen as the optimum temperature of BPB and BPZMB, and a temperature of 25 °C was chosen as the optimum temperature of BPZB and BPMB. The optimum material dosage, contact time, and temperature of each material were applied to study the pH effect.

For the pH effect, the reuslts are shown in Fig. [7](#page-11-0)e. The increase of pH affected the increase of cadmium removal efficiencies of BPB, BPZB, BPMB, and BPZMB from pH 3–5, and then they were stable which was similarly found in previous studies that the high cadmium adsorption at  $pH > 5^{7,25}$  $pH > 5^{7,25}$  $pH > 5^{7,25}$  $pH > 5^{7,25}$ . In addition, the results also corresponded to their  $pH_{pzc}$  values were in a range of  $pH$  5–10, so cadmium(II) ions could be adsorbed in those ranges while observing the stable cadmium removal efficiency. As a result, cadmium(II) ions could be adsorbed by all materials in a wide pH range from pH 5–10. Therefore, pH 5 was the optimum pH of all materials for obtaining the highest cadmium removal efficiency at 90.80%, 97.05%, 99.88%, and 98.34% for BPB, BPZB, BPMB, and BPZMB, respectively. The optimum material dosage, contact time, temperature, and pH of each material were applied to study the initial concentration effect.

For the initial concentration effect, the results are demonstreated in Fig. [7f](#page-11-0). The increase of initial cadmium concentration from 25 to 200 mg/L resulted in the decrease of cadmium removal efficiencies of BPB, BPZB, BPMB, and BPZMB resulting from the decrease of the available adsorbent pore of material similar reported by previous studies<sup>14,20</sup>. For the initial cadmium concentration of 100 mg/L, the cadmium removal efficiencies of BPB, BPZB, BPMB, and BPZMB were 89.18%, 96.62%, 99.59%, and 97.85%, respectively.

In conclusion, the optimum conditions of material dosage, contact time, temperature, pH, and initial concentration of BPB, BPZB, BPMB, and BPZMB were 0.2 g, 8 h, 35 °C, pH 5, and 100 mg/L for 89.18%, 0.08 g, 5 h, 25 °C, pH 5, and 100 mg/L for 96.62%, 0.04 g, 5 h, 25 °C, pH 5, and 100 mg/L for 99.59%, and 0.06 g, 5 h, 35 °C, pH 5, and 100 mg/L for 97.85%, respectively which BPMB demonstrated a higher potential material than other materials because of spending less material dose than others with 99.59% cadmium removal efficiency. In addition, it could be arranged from high to low cadmium removal efficiency to be BPMB > BPZMB > BPZB > BPB. Therefore, the banana materials with ZnO or MgO modification increased material efficiency, especially MgO, and the material modification with ZnO and MgO in 50:50 ratios (BPZMB) illustrated a higher cadmium removal efficiency than banana material with or without ZnO modification.

#### **Adsorption isotherms**

The adsorption patterns of BPB, BPZB, BPMB, and BPZMB were investigated through the adsorption isotherms. Four isotherm models of Langmuir, Freundlich, Temkin, and Dubinin-Radushkevich in both linear and nonlinear models were used to determine which model was the better model to describe their adsorption patterns on cadmium adsorptions with choosing a high  $R^2$  close to be 1.

Figure [8](#page-13-0)a-h demonstrated their plotting results, and Table [7](#page-14-0) illustrated their adsorption isotherm parameters. Since  $R^2$  values in linear and nonlinear Freundlich models of all materials were higher than other models, their adsorption patterns corresponded to the Freundlich model relating to a multilayer adsorption process. For the adsorption intensity  $(n)$ ,  $1/n$  values in linear and nonlinear models of all materials were in a range of  $0 < 1/n < 1$ which meant they favored cadmium adsorptions<sup>[21](#page-21-0),44</sup>. For the Freundlich constant  $(K_c)$ , BPMB had a higher  $K_c$ value than other materials in both linear and nonlinear models, so it could strongly adsorb cadmium on BPMB.

The maximum adsorption capacity (*q*m) comparison with previous studies that used banana peels for cadmium removal with or without modifications is demonstrated in Table [8.](#page-14-1) All materials in this study had higher  $q_m$  values than all previous studies in Table [8](#page-14-1) except BPB had a lower  $q_m$  value than the study of Ge et al.<sup>7</sup> and Chen et al.<sup>47</sup>. Therefore, all materials in this study were potential materials for eliminating cadmium(II) ions in wastewater with the high  $q_m$  values especially BPMB demonstrated the highest  $q_m$  value of 454.55 mg/g than other materials. In the case of correct data translation, linear and nonlinear models are recommended to use for rechecking the correct results similar to other studies  $48,44$ .

<span id="page-13-0"></span>

**Fig. 8**. Graphs of (a) linear Langmuir, (b) linear Freundlich, (c) linear Temkin, (d) linear Dubinin-Radushkevich, and nonlinear adsorption isotherms (e) BPB, (f) BPZB, (g) BPMB, and (h) BPZMB for cadmium adsorptions.

#### **Adsorption kinetics**

The adsorption rates and mechanisms of BPB, BPZB, BPMB, and BPZMB were investigated through the adsorption kinetics. Four kinetic models of pseudo-first-order kinetic, pseudo-second-order kinetic, Elovich, and intraparticle diffusion in both linear and nonlinear models were used to determine which model was better model to describe their adsorption rates and mechanisms on cadmium adsorptions with choosing a high *R*<sup>2</sup>

<span id="page-14-0"></span>

**Table 7**. Linear and nonlinear isotherm parameters for cadmium adsorptions on BPB, BPZB, BPMB, and BPZMB.

<span id="page-14-1"></span>

**Table 8**. The maximum adsorption capacity of banana adsorbents for cadmium adsorption.

close to be 1. Similar to adsorption isotherms, the linear and nonlinear models were applied for rechecking the results.

Figure [9a](#page-15-0)-h demonstrated their plotting results, and Table [9](#page-16-0) illustrated their adsorption kinetic parameters. The pseudo-second-order model was the best-fit model for all materials with a higher  $R^2$  value than other kinetic models both in linear and nonlinear models, so their adsorption rates and mechanisms were a chemisorption

<span id="page-15-0"></span>

**Fig. 9**. Graphs of (a) linear pseudo-first-order, (b) linear pseudo-second-order, (c) linear Elovich (d) linear intraparticle diffusion, and nonlinear kinetic models of (e) BPB, (f) BPZB, (g) BPMB, and (h) BPZMB for cadmium adsorptions.

<span id="page-16-0"></span>

**Table 9**. Linear and nonlinear kinetic parameters for cadmium adsorptions on BPB, BPZB, BPMB, and BPZMB.

process agreed with other previous studies<sup>14,42</sup>. The comparing cadmium adsorption capacity  $(q_e)$  and pseudosecond-order kinetic rate constant  $(k_2)$  in a pseudo-second-order model, BPMB had a higher both  $q_e$  and  $k_2$  in both linear and nonlinear models than other materials, so it might be a higher cadmium adsorption with a fast adsorption rate than others. In addition, it could be a range from high to low of  $q_e$  and  $k_2$  to be BPMB>BPZMB>BPZB>BPB. Moreover, the results also corresponded to batch tests that BPMB had higher cadmium adsorption than BPB, BPZB, and BPZMB.

#### **Thermodynamic study**

Since the changing temperature may affect to cadmium removal efficiency of materials, the thermodynamic study is used to investigate how it affects. The results are demonstrated in Table [10](#page-17-0), and their thermodynamic plots for cadmium adsorptions are shown in Fig. [10a](#page-17-1)-d. The ∆*G*˚ values of all materials were negative which means their cadmium adsorptions could occur in a spontaneous nature, so the increase in temperature did not favor their cadmium adsorptions. In addition, their ∆*H*˚ were negative representing an exothermic process in nature. Since they were in a range of (-20) – (-80) kJ/mol, they were physical and chemical adsorption processes<sup>[31](#page-21-10)</sup>. For  $\Delta S^{\circ}$ , they were negative which meant the decrease of the randomness during the adsorption process<sup>44</sup>.

#### **Material reusability**

Before the materials are applied in industrial plants, it is necessary to test the efficiency of the material to see how many times it can be reused to be worth the investment through the desorption experiments. Three adsorption-desorption cycles were used for studying the material efficiencies of BPB, BPZB, BPMB, and BPZMB for cadmium removals, and their results are demonstrated in Fig. [11.](#page-18-0) Their cadmium removal efficiencies were

<span id="page-17-0"></span>

#### **Table 10**. Thermodynamic parameters of BPB, BPZB, BPMB, and BPZMB for cadmium adsorptions.



<span id="page-17-1"></span>

Fig. 10. Thermodynamic plots of (a) BPB, (b) BPZB, (c) BPMB, and (d) BPZMB for cadmium adsorptions.

<span id="page-18-0"></span>

**Fig. 11**. Material reusability by desorption experiments of BPB, BPZB, BPMB, and BPZMB.

more than 73% after they were used in 3 cycles. Especially, BPMB had a cadmium removal efficiency of more than 81% after reusing 3 cycles. In addition, their cadmium removal efficiencies were approximately decreased by 10% for each cycle. Therefore, all materials are potentially applied in industrial wastewater treatment.

#### **The possible mechanisms of cadmium adsorptions**

The main possible process of electrostatic interaction could be used to explain adsorption mechanisms by BPB, BPZB, BPMB, and BPZMB which modified the idea from our previous study<sup>24</sup> are demonstrated in Fig. [12](#page-19-0). Since banana peels composed of cellulose and lignin, they consisted of the hydroxyl group (–OH) which they could adsorb cadmium(II) ions through the electrostatic interaction by instead of the proton  $(H^+)$  by cadmium(II) ions. In addition, cadmium(II) ions are also adsorbed through the sharing electron of –OH and the complex compounds of banana peels and ZnO or MgO on the surface of BPZB, BPMB, and BPZMB through the electrostatic interaction.

#### **The cost-effectiveness analysis**

Before industrial uses, the cost-effectiveness analysis is an important issue in estimating whether a material is worth its use and investment. Generally, the choice of adsorbent is based on the availability of raw material,

<span id="page-19-0"></span>

**Fig. 12**. Possible mechanisms of cadmium adsorptions by BPB, BPZB, BPMB, and BPZMB.

synthesis method, reusability, and usage. Since banana peels are waste, so there is no cost for raw materials. The chemical uses and synthesis methods of BPB, BPZB, BPMB, and BPZMB are suitable prices and simple synthesis steps. The material costs were approximately \$20 per kg per material which referred from a previous study that used lemon peels for synthesizing beaded materials modified with ZnO or iron(III) oxide-hydroxide for reactive blue 4 dye removals<sup>46</sup>. Moreover, they could be reused in 3 cycles with a cadmium removal efficiency of more than 73%, so they helped to save an operation cost. Since they are beaded materials, they are easier to separate than powder materials. Therefore, they are good materials for adsorbing cadmium(II) ions for industrial applications.

### **Conclusion**

- The novel cadmium adsorbents of banana powder beads (BPB), banana powder doped ZnO beads (BPZB), banana powder doped MgO beads (BPMB), and banana powder doped ZnO+MgO beads (BPZMB) were successfully synthesized by banana peels and two metal oxide of zinc and magnesium.
- The addition of ZnO or MgO into banana peels increased the specific surface area and pore volume of materials resulting in increasing the cadmium adsorption capacity of material, especially BPMB.
- XRD, EDX, and FT-IR techniques could confirm the ability of ZnO or MgO additions into BPZB or BPMB or BPZMB because they detected the specific peaks of ZnO or MgO, the chemical elements of zinc or magnesium, and the functional groups of Zn–O or Mg–O.
- The pH<sub>pzc</sub> values of BPB, BPZB, BPMB, and BPZMB were 5.37, 6.75, 9.87, and 9.43, so ZnO and MgO increased the  $pH_{pzc}$  of material, especially MgO.
- BPMB demonstrated a higher cadmium removal efficiency of 99.59% than other materials with spending less material dosage than others. Therefore, the metal oxide helped to improve material efficiency, especially MgO.
- The maximum adsorption capacities (*q*m) of BPB, BPZB, BPMB, and BPZMB were 90.09, 232.56, 454.55, and 303.03 mg/g which they had higher  $q_m$  values than other previous studies that used banana peels as raw material for adsorbing cadmium(II) ions in aqueous solution.
- They could be reused for more than 3 cycles with high cadmium adsorption of more than 73%.
- They were novel materials that used the simple step of material synthesis, suitable cost, easy use and separation after treatment, and capable of reusability responding to the worth use and investment. They also offered high performances for cadmium adsorption, so they were good choices of adsorbents for applying industry.

For future works, the continuous flow study should be investigated before being applied in industrial applications, and the competing anionic ions might be studied to confirm the specific target adsorption of materials. Moreover, real wastewater containing cadmium ions needs to be investigated to confirm their abilities for cadmium removal.

#### **Data availability**

The datasets used and/or analyzed during the current study are available from the corresponding author upon reasonable request.

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#### **Competing interests**

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#### **Additional information**

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