

Phosphoric acid-modified banana peel and rice straw as low-cost sorbents for the removal of Pb(II) and Cu(II) from aqueous solution

Pham Hoang Giang^{1*}, Do Quang Huy¹, Phan Quang Hung², Nguyen Ha Dan Khanh³

¹VNU University of Science, Vietnam National University, Hanoi, Vietnam

E-mail: phamhoang.giang@hus.edu.vn

Email: huy.doquang.vnu@gmail.com

²British International School, Ho Chi Minh City, Vietnam

Email: hungquangphan2008@gmail.com

³Bui Thi Xuan High School, Ho Chi Minh City, Vietnam

Email: dankhanhnguyenha@gmail.com

*Corresponding author

Abstract: Agricultural by-products are attractive precursors for low-cost heavy-metal sorbents, yet their native binding capacity is usually modest and comparative data for materials treated under one and the same modification protocol remain scarce. In the present study, eight by-products collected around Hanoi, Vietnam — sugarcane bagasse, banana peel, coir, sawdust, corn husk, rice husk, rice straw and peanut shell — were esterified with H_3PO_4 in the presence of urea and screened for cation-exchange capacity using methylene blue as a cationic probe. Phosphoric acid modification raised methylene blue removal by a factor of 1.6–5.0 relative to the corresponding unmodified material, and the two best performers, modified banana peel (79.44%) and modified rice straw (81.75%), were selected for batch adsorption of Pb^{2+} and Cu^{2+} . Scanning electron micrographs showed that the outer layer of both materials was disrupted by the treatment, exposing the underlying fibre bundles. Metal uptake increased with pH up to the working value of pH 5, and equilibrium was reached within 60–180 min. The equilibrium data were described better by the Langmuir ($R^2 > 0.91$) than by the Freundlich model ($R^2 \leq 0.88$), giving maximum capacities (Q_{max}) of 121.95 mg Pb^{2+} /g and 53.2 mg Cu^{2+} /g for modified banana peel, and 55.56 mg Pb^{2+} /g and 46.3 mg Cu^{2+} /g for modified rice straw; except for Pb^{2+} on modified rice straw, these values lie beyond the highest measured uptake and are therefore upper estimates. These findings identify phosphorylated banana peel as the more promising of the two sorbents and warrant further work on sorbent characterisation, regeneration and real wastewater.

Keywords: Adsorption; Agricultural by-products; Banana peel; Heavy metals; Phosphoric acid modification; Rice straw; Wastewater treatment

1. Introduction

Over the past few decades, rapid economic development and population growth have placed increasing pressure on the environment, and heavy-metal contamination of water is among the most persistent of the resulting problems. Industrial and domestic activities release large quantities of toxic metals into soil and water; unlike organic pollutants, these metals are not degraded, accumulate along the food chain and ultimately affect human health [1]. Recent assessments of heavy-metal water pollution continue to rank it among the priority hazards, precisely because of this combination of toxicity, persistence and bioaccumulation [2], [3]. Lead and copper are typical of the metals discharged by electroplating, metallurgical, mining and battery-related activities, and were therefore chosen as the target ions of this work. The removal of heavy metals from water has consequently become an intensively studied topic. The technologies in common use include chemical precipitation, ion exchange, adsorption, membrane filtration, coagulation–flocculation and electrochemical treatment [4]. More recent critical reviews group the available options into adsorption-, membrane-, chemical-, electric- and photocatalytic-based treatments and reach a similar verdict:

each has a characteristic weakness — sludge generation, membrane fouling, energy demand or reagent cost — and no single method is superior in both removal efficiency and cost [3], [5]. Among them, adsorption is generally regarded as the most accessible for decentralised or small-scale use because of its simple operation and the wide choice of sorbents, provided that the sorbent itself is inexpensive [3].

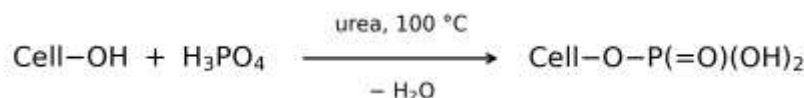
For this reason, the use of natural materials and agricultural by-products as sorbents for heavy metals has attracted sustained interest, both for economic reasons and for the removal efficiency that can be achieved. Studies worldwide and in Vietnam have examined orange peel [6], macroalgae [7], biochars [8]–[10], peanut shell [11], aquatic plants [12], coir [13], [14] and rice husk [13], with encouraging initial results. Over the last five years the field has moved strongly towards thermally converted products, in particular biochars and hydrochars and their composites [15], while raw or mildly treated residues have continued to be examined for the same two metals studied here — for example, native banana peel for Cu(II) and Pb(II) in single and binary systems [16] and straw-derived biochar composites for Cu(II) and Pb(II) [17]. Chemical modification at low temperature remains attractive

because it avoids the energy cost of pyrolysis and preserves the fibrous form of the material.

The main chemical constituents of natural fibres are cellulose (30–91%), hemicellulose (4–16%) and lignin (0.6–26%) [18], [19]. These polymers carry abundant hydroxyl groups, which can be esterified with phosphoric acid (Scheme 1) [20]. Gong et al. [20] showed that the phosphate groups introduced by esterification increase the cation-exchange capacity of the natural fibre, as demonstrated for the sorption of basic dyes on phosphoric acid-modified rice straw. Phosphate functionalisation has since been applied to other lignocellulosic residues for metal removal, for instance ramie stalk for Zn^{2+} [21], and phosphoric acid has also been used as a modifier in the hydrothermal carbonisation of banana peel for Pb(II) sorption [22]. Together, these reports point to the potential of phosphoric acid-modified natural fibres as sorbents for heavy metals.

Nevertheless, comparative information remains limited. Most studies deal with a single feedstock, so that capacities

obtained under different modification procedures, sorbent doses and concentration ranges cannot be compared directly, and data for by-products available in northern Vietnam are still scarce. Against this background, the aims of the present work were (i) to modify eight agricultural by-products collected around Hanoi with H_3PO_4 under a single protocol and to rank them by their uptake of methylene blue, used as a probe of cation-exchange capacity; (ii) to examine by scanning electron microscopy (SEM) the effect of the modification on the surface of the two best materials; and (iii) to determine the influence of pH, contact time and initial concentration on the adsorption of Pb^{2+} and Cu^{2+} on these two materials and to describe the equilibrium data with the Langmuir and Freundlich models. The modification procedure itself is that of Gong et al. [20]; the novelty here lies in its side-by-side application to eight local by-products and in the Pb^{2+} and Cu^{2+} capacities of the phosphorylated banana peel and rice straw.



Scheme 1. Esterification of the hydroxyl groups of cellulose with phosphoric acid [20].

2. Materials and methods

2.1. Materials and chemicals

The agricultural by-products — sugarcane bagasse, banana peel, coir, sawdust, corn husk, rice husk, rice straw and peanut shell — were collected from areas around Hanoi, Vietnam. H_3PO_4 (85%), acetone, urea, NaOH, 70% ethanol, methylene blue, $\text{Pb(NO}_3)_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ were of analytical grade and were supplied by Merck (Germany). Stock solutions of Pb^{2+} and Cu^{2+} were prepared from $\text{Pb(NO}_3)_2$ and $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, respectively. Deionised distilled water was used throughout.

2.2. Preparation of the unmodified material

The samples were washed with distilled water and soaked in 0.02 M NaOH for 30 min to remove impurities, then dried at 60 °C and cut into fibres 0.5 cm in length to give the unmodified (raw) material.

2.3. Phosphoric acid modification

The modification followed the procedure of Gong et al. [20]. A 5.43 g portion of the sample was soaked in acetone overnight, washed with distilled water and soaked again in acetone for 6 h. The sample was filtered and dried at 50–60 °C for 4–5 h. It was then suspended in 200 mL of acetone, 5.04 g of urea was added with stirring, and H_3PO_4 (3.1 g) was added dropwise during stirring. After stirring for 1 h, the acetone was removed, the temperature was raised to 100 °C and stirring was

continued for 2 h. The sample was cooled to room temperature and filtered, washed with 70% ethanol and distilled water, and stirred in 0.1 M NaOH. After 1 h it was washed again with distilled water and dried at 50 °C for 24 h to give the modified material. The raw and modified samples of the two selected materials were ground for SEM observation.

2.4. Screening of cation-exchange capacity with methylene blue

A 0.5 g portion of the raw or modified material was placed in 200 mL of methylene blue solution (0.5 g/L) at pH 7 and shaken for 2 h. The dye loading was therefore 100 mg per 0.5 g of sorbent, at a solid-to-liquid ratio of 2.5 g/L, which corresponds to 0.625 mmol of dye per gram of sorbent if all of the dye were taken up. The test is used here as a relative screen for cationic-dye uptake and not as a measurement of cation-exchange capacity, for the reason set out in Section 3.1. The two materials with the highest uptake were selected for the heavy-metal adsorption experiments.

2.5. Batch adsorption of Pb^{2+} and Cu^{2+}

Batch experiments were carried out to examine the factors influencing the adsorption of Pb^{2+} and Cu^{2+} on the selected materials, namely contact time, pH and initial metal concentration. The effect of pH was studied over pH 1–5 at initial concentrations of 333 mg/L Pb^{2+} and 353 mg/L Cu^{2+} ; the effect of initial concentration was studied over 10.926–382.41 mg/L for Pb^{2+} and 10–353.1 mg/L for Cu^{2+} . To ensure optimal adsorption measurement across different systems, the sorbent dosages (m/V) were set at 2.9 g/L for Pb^{2+} on modified banana

peel, 3.3 g/L for Pb²⁺ on modified rice straw, 2.3 g/L for Cu²⁺ on modified banana peel, and 1.6 g/L for Cu²⁺ on modified rice straw.

The removal efficiency H (%) and the amount adsorbed q (mg/g) were calculated as:

$$H = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e) \times V}{m} \quad (2)$$

where C_0 and C_e (mg/L) are the initial and equilibrium metal concentrations, V (L) is the solution volume and m (g) is the mass of sorbent. The equilibrium data were evaluated with the linearised forms of the Langmuir [23] and Freundlich [24] models,

$$\frac{C_e}{q_e} = \frac{1}{K_L Q_{\max}} + \frac{C_e}{Q_{\max}} \quad (3)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (4)$$

where $Q_{\max}$ (mg/g) is the maximum monolayer capacity, K_L (L/mg) is the Langmuir constant, and K_F and $1/n$ are the Freundlich constants.

2.6. Analytical methods

The surface morphology of the materials was examined with an FEI Nova NanoLab 200 scanning electron microscope at the Faculty of Physics, VNU University of Science, Hanoi. Metal concentrations were determined by atomic absorption spectrometry (Pye Unicam SP9, UK) at the Geological Analysis Centre. Methylene blue was determined on an L-VIS-400 spectrophotometer at the Faculty of Environmental Sciences, VNU University of Science.

3. Results and discussion

3.1. Cation-exchange capacity of the raw and modified materials

Table 1 gives the methylene blue removal efficiency of the raw and modified materials. After modification with phosphoric acid, all eight materials removed markedly more methylene blue than the corresponding raw material, by a factor of 1.6 (coir, corn husk) to 5.0 (sawdust), which indicates that the phosphate groups introduced by the treatment increased the total number of anionic sites. This in turn suggests an enhanced capacity for heavy-metal cations. Expressed as uptake, these efficiencies correspond to 21.3–96.1 mg/g for the raw materials and 65.7–163.5 mg/g for the modified materials (Table 1). The two modified materials with the highest methylene blue removal, banana peel (79.44%) and rice straw (81.75%), were selected for the heavy-metal experiments. Two features of the screen limit what it can establish. First, the dye loading corresponds to 0.625 mmol/g, whereas the charge equivalents implied by the copper capacities reported in Section 3.3.3 are 1.67 and 1.46 meq/g for the two selected materials; the test is therefore limited by the amount of dye supplied rather than by the sorbent, and the three leading materials (76.36, 79.44 and 81.75%) lie within 5.4 percentage points of one another close to complete removal, where the measurement cannot discriminate between them. Second, the dye occupies only 0.50 and 0.51 meq/g on the two selected materials, that is about a third of the equivalents occupied by copper, so the dye does not report the same population of sites as the metal ions. The screen is accordingly a relative ranking of cationic-dye uptake, and Section 3.4 shows that it does not predict the lead capacity.

Table 1. Methylene blue removal efficiency of the raw and phosphoric acid-modified materials (0.5 g sorbent, 200 mL of 0.5 g/L methylene blue, pH 7, 2 h).

Material	Raw (%)	Modified (%)	Modified / raw ^a	q raw (mg/g)	q modified (mg/g)
Sugarcane bagasse	14.39	43.51	3.0	28.8	87.0
Banana peel	30.35	79.44	2.6	60.7	158.9
Coir	48.04	76.36	1.6	96.1	152.7
Sawdust	10.65	52.85	5.0	21.3	105.7
Corn husk	38.26	61.18	1.6	76.5	122.4
Rice husk	9.65	42.92	4.4	19.3	85.8
Rice straw	36.10	81.75	2.3	72.2	163.5
Peanut shell	17.77	32.86	1.8	35.5	65.7

^aCalculated from the two preceding columns. Uptake q was calculated as (removal efficiency/100) $\times$ 100 mg / 0.5 g, from the dye loading and sorbent mass given in Section 2.4.

3.2. Effect of modification on surface morphology

The SEM images of rice straw before and after modification (Fig. 1) show that the raw straw had a grooved surface bearing nodular protrusions, whereas the modified straw had a fibre-bundle appearance: the outer layer had been broken down completely, exposing the inner fibres. Figure 2 shows that the surface of the modified banana peel had likewise changed relative to the raw material, the outer layer having been disrupted. The modification

thus altered the surface structure of both materials in a way that is expected to increase the accessible surface area and, with it, the uptake of the dye.

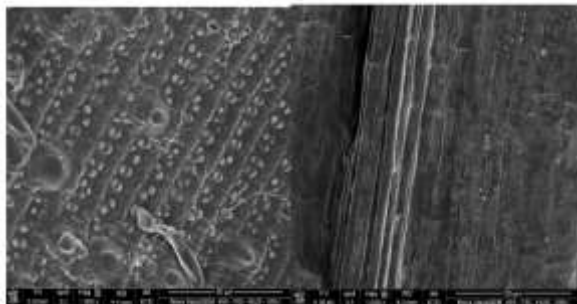


Figure 1. SEM images of raw (left) and phosphoric acid-modified (right) rice straw.

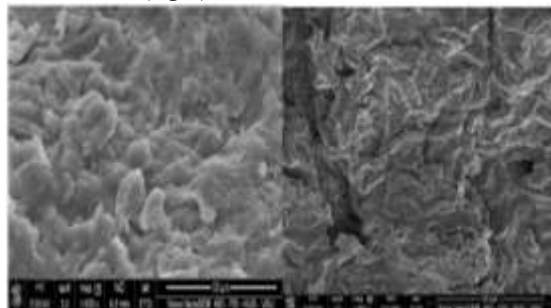


Figure 2. SEM images of raw (left) and phosphoric acid-modified (right) banana peel.

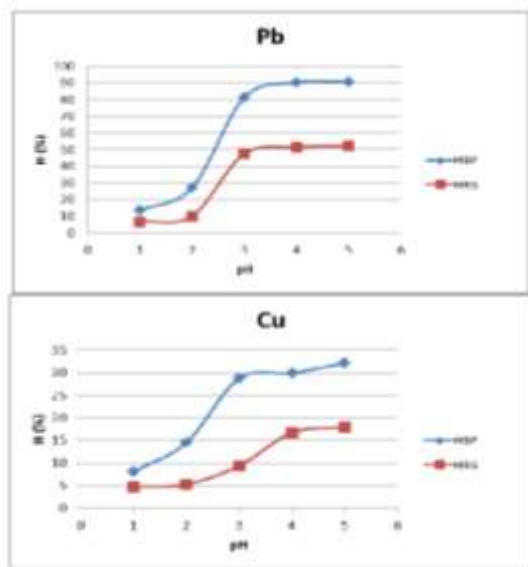


Figure 3. Effect of pH on the removal efficiency of Pb^{2+} (top) and Cu^{2+} (bottom). MBP, modified banana peel; MRS, modified rice straw.

3.3.2. Effect of contact time

The effect of contact time is shown in Fig. 4. Equilibrium was reached after 180 min for Pb^{2+} and 120 min for Cu^{2+} on modified banana peel, and after 60 min for both metals on modified rice straw.

3.3. Factors influencing the adsorption of Pb^{2+} and Cu^{2+}

3.3.1. Effect of pH

The effect of pH over the range 1–5 on adsorption at initial concentrations of 333 mg/L Pb^{2+} and 353 mg/L Cu^{2+} is shown in Fig. 3. The removal efficiency increased with pH. At low pH the efficiency was low and rose only slightly, which can be explained by competition between H^+ and the metal ions for the binding sites. In most cases the efficiency no longer changed above pH 4, the exception being Cu^{2+} on modified banana peel. The experiments were not extended beyond pH 5 because the two metals begin to precipitate as hydroxides above this pH at the concentrations used.

Taking $[OH^-] = \left(\frac{K_{sp}}{[M^{2+}]}\right)^{1/2}$, with $K_{sp} = 1.4 \times 10^{-20}$ for $Pb(OH)_2$ and 2.2×10^{-20} for $Cu(OH)_2$, precipitation begins at approximately pH 5.5 for Pb^{2+} at 333 mg/L (1.61 mM) and at approximately pH 5.3 for Cu^{2+} at 353 mg/L (5.56 mM); at the highest lead concentration used, 382.41 mg/L, the threshold falls to approximately pH 5.4. The margin at pH 5 is thus about half a pH unit for lead and about 0.3 units for copper, and pH 5 was adopted for the subsequent experiments.

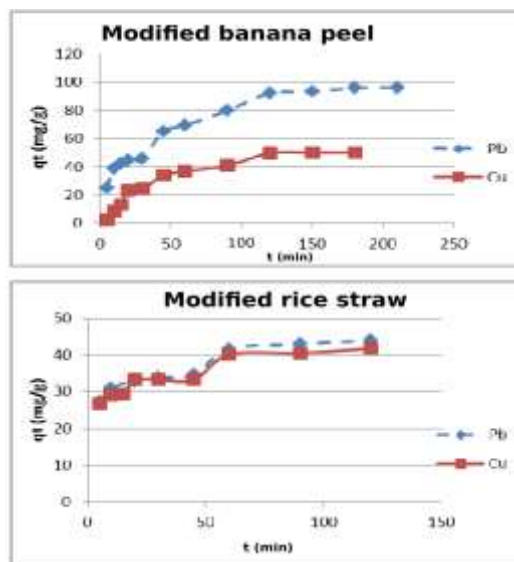


Figure 4. Effect of contact time on the amount of Pb^{2+} and Cu^{2+} adsorbed (q_t) by modified banana peel (top) and modified rice straw (bottom).

3.3.3. Effect of initial concentration and adsorption isotherms

The uptake of the two metal ions was examined at different initial concentrations (Pb^{2+} : 10.926–382.41 mg/L; Cu^{2+} : 10–353.1 mg/L) (Fig. 5), and the results were fitted to the Langmuir and Freundlich isotherms (Tables 2 and 3). In all four systems the data correlated well with the Langmuir model ($R^2 > 0.91$), whereas the correlation coefficients for the Freundlich model were low, the highest being 0.87 for Cu^{2+} on modified banana peel. According to the Langmuir equation, modified

banana peel had the highest maximum capacity, 121.95 mg/g for Pb^{2+} , more than twice that of modified rice straw (55.56 mg/g). Modified banana peel also had the higher capacity for Cu^{2+} : 53.2 mg/g as against 46.3 mg/g for modified rice straw.

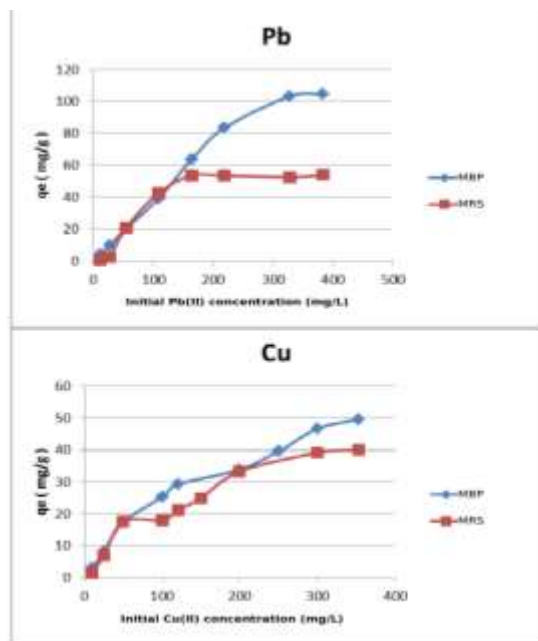


Figure 5. Effect of initial metal concentration on the amount of Pb^{2+} (top) and Cu^{2+} (bottom) adsorbed (q_e). MBP, modified banana peel; MRS, modified rice straw.

Table 2. Langmuir isotherm parameters for the two modified materials.

Material	Pb^{2+}		Cu^{2+}	
	R^2	$Q_{\max}$ (mg/g)	R^2	$Q_{\max}$ (mg/g)
Modified banana peel	0.9458	121.95	0.9638	53.2
Modified rice straw	0.9975	55.56	0.9118	46.3

Table 3. Freundlich isotherm parameters for the two modified materials.

Material	Pb^{2+}		Cu^{2+}	
	K_F	R^2	K_F	R^2
Modified banana peel	13.842	0.5728	3.54	0.8743
Modified rice straw	27.289	0.5841	9.486	0.6901

3.4. Comparison with previous studies

Capacity relative to related sorbents. Table 4 places the present capacities alongside values reported for closely related materials. Native banana peel is a weak sorbent for lead: Anwar et al. reported a Langmuir capacity of only 2.18 mg Pb/g [25], so that the value obtained here for the phosphorylated peel is higher by well over an order of magnitude. It is also of the same order as the values reported recently for H_3PO_4 -modified banana peel hydrothermal carbon, a material synthesised at a hydrothermal temperature of 240 °C: the Langmuir capacity of that sorbent was 76.54 mg/g at 293 K, 88.94 mg/g at 303 K and 103.24 mg/g at 313 K, and the capacity quoted for its optimum operating point was 40.64 mg/g [22]. The present material was obtained at ≤ 100 °C without carbonisation. For rice straw, the

capacities of the phosphorylated fibre (55.56 mg Pb/g; 46.3 mg Cu/g) are comparable with the 46.98 mg Pb/g and 60.86 mg Cu/g reported for a straw biochar–sludge composite pyrolysed at 500 °C [17]. Both materials remain well below the most heavily functionalised biosorbents, such as graft-copolymerised orange peel (476.1 mg Pb/g) [6], whose preparation is, however, considerably more elaborate. Such comparisons must be read with caution, since the studies differ in sorbent dose, concentration range, pH and fitting method; they nonetheless indicate that low-temperature phosphorylation can bring raw lignocellulosic residues into the capacity range of thermally converted sorbents, which is of practical interest where pyrolysis facilities are unavailable.

Table 4. Langmuir maximum capacities (mg/g) of the modified materials compared with related sorbents from the literature.

Sorbent	Pb(II)	Cu(II)	Conditions	Ref.
Phosphoric acid-modified banana peel	121.95	53.2	pH 5	This work
Phosphoric acid-modified rice straw	55.56	46.3	pH 5	This work
Native banana peel	2.18	–	batch	[25]
Graft-copolymerised orange peel	476.1	–	batch	[6]
H ₃ PO ₄ -modified banana peel hydrothermal carbon (240 °C)	103.24	–	1 g/L sorbent, 313 K	[22]
Straw biochar–sludge composite (500 °C)	46.98 ^a	60.86 ^a	batch	[17]

^aMaximum equilibrium uptake; the Freundlich model gave the better fit in that study.

Mass versus molar basis. Expressed in mg/g, both materials appear to favour lead. On a molar basis the order is reversed: the $Q_{\max}$ values correspond to 0.59 mmol Pb/g and 0.84 mmol Cu/g for modified banana peel, and to 0.27 mmol Pb/g and 0.73 mmol Cu/g for modified rice straw (atomic masses 207.2 and 63.55). More binding sites are therefore occupied by copper than by lead, and the higher mass-based capacity for lead reflects mainly its higher atomic mass. A higher mass-based uptake of Cu(II) than of Pb(II) has in fact been reported for a straw biochar composite [17], which shows that the Pb > Cu order often quoted for biosorbents is not general. The difference between the two materials is also instructive: their molar capacities for copper are similar (0.84 and 0.73 mmol/g), in keeping with their nearly identical methylene blue removal (79.44 and 81.75%), whereas the capacity for lead is more than twice as high on banana peel. This suggests that the phosphorylated banana peel offers additional sites accessible to Pb²⁺ — a hypothesis that remains to be tested by surface analysis. The comparison with the dye is instructive in the same way. On a charge-equivalent basis the two materials take up 0.50 and 0.51 meq/g of methylene blue but 1.67 and 1.46 meq/g of copper, so the metal occupies between 2.9 and 3.4 times the equivalents occupied by the dye. Steric exclusion of the bulky dye cation accounts for part of this difference, but the ratio also shows that the dye and the metal do not address a common set of exchange sites, which is the direct reason why the dye ranking does not reproduce the ranking by lead capacity.

Effect of pH and mechanism. The steep rise in removal between pH 2 and 4 and the plateau at pH 4–5 agree with the behaviour reported for Pb(II) on H₃PO₄-modified banana peel hydrochar, where uptake rose from pH 2 and peaked at pH 6, with ion exchange, electrostatic attraction and surface complexation proposed as the operating mechanisms [22], and with the choice of pH 5.5 for Cu(II) and Pb(II) on native banana peel, whose point of zero charge was 4.83 [16]. For a phosphorylated fibre, progressive deprotonation of the grafted phosphate groups over this pH range offers a straightforward explanation of the trend, consistent with the cation-exchange role assigned to these groups by Gong et al. [20] and with the phosphate-mediated binding of Zn²⁺ on functionalised ramie stalk [21]. In the absence of spectroscopic evidence for the present materials, this interpretation should be regarded as a working hypothesis.

Contact time. Modified rice straw reached equilibrium within 60 min, whereas modified banana peel required 120–180 min. For comparison, Pb(II) uptake on H₃PO₄-modified banana peel hydrochar occurred mainly within the first 60 min but levelled off only after about 250 min [22]. The slower approach to equilibrium on banana peel is compatible with its higher capacity and with a contribution from less accessible sites, but no kinetic model was fitted to the present data.

Isotherm fitting. The preference for the Langmuir over the Freundlich model is in line with the H₃PO₄-modified banana peel hydrochar [22], whereas the straw biochar composite was better described by the Freundlich model [17]. Current guidelines, however, caution against model selection based on the R² of linearised equations alone: linearisation alters the error structure of the data and can bias the fitted parameters, and non-linear regression with appropriate error functions is recommended [26], [27].

This caveat applies to the present results, which were obtained from the linearised equations. The experimental plateaux in Fig. 5 lie at approximately 105 mg/g (Pb^{2+} , banana peel) and 54 mg/g (Pb^{2+} , rice straw); the Langmuir Q_{max} of 55.56 mg/g is thus well supported for rice straw, whereas that of 121.95 mg/g for banana peel ($R^2 = 0.9458$) is an extrapolation beyond the measured range and should be treated as an upper estimate. The Cu^{2+} isotherms had not reached a plateau at the highest concentration tested, so the corresponding Q_{max} values are similarly extrapolated.

3.5. Limitations and outlook

Several limitations temper these conclusions and frame the next steps. First, the modified materials were characterised only by SEM, which is qualitative; the increase in surface area inferred from the micrographs was not measured (BET), and the grafting of phosphate groups was not verified by FTIR, elemental phosphorus content or determination of the point of zero charge. Second, the raw materials used as controls were washed only with 0.02 M NaOH, whereas the modified materials were additionally extracted with acetone and treated with 0.1 M NaOH; part of the gain in methylene blue uptake may therefore stem from solvent and alkali treatment rather than from phosphorylation, and a control carried through the procedure without H_3PO_4 would resolve this. Third, methylene blue removal was measured at a single concentration and is a ranking tool rather than a capacity; as shown in Section 3.1, the dye loading of 0.625 mmol/g is below the equivalents that the two best materials were subsequently shown to occupy, so the screen was limited by the dye supplied and could not resolve the leading materials from one another. A screen designed so that removal falls between about 20 and 60%, or a full dye isotherm, would be required for a quantitative comparison. Fourth, the isotherm constants K_L and $1/n$ and the standard deviations of the triplicate measurements were not reported, and the kinetic data were not modelled. Finally, desorption and reuse, competing ions and real wastewater were beyond the scope of this study; they are the natural objectives of follow-up work, together with fixed-bed experiments of the kind already reported for other phosphate-functionalised residues [21].

4. Conclusions

Modified sorbents were prepared from banana peel and rice straw by treatment with H_3PO_4 . SEM images showed that the modification changed the surface structure of the materials, which is expected to increase the accessible surface area and hence the adsorption capacity. All eight phosphoric acid-modified by-products removed more methylene blue than the corresponding raw materials (by a factor of 1.6–5.0), modified banana peel and modified rice straw giving the highest removal. The adsorption of Pb^{2+} and Cu^{2+} at pH 5 followed the Langmuir isotherm, with maximum capacities (Q_{max}) of 121.95 mg Pb^{2+} /g and 53.2 mg Cu^{2+} /g for modified banana peel, and 55.56 mg Pb^{2+} /g and 46.3 mg Cu^{2+} /g for modified rice straw. Only the lead capacity of modified rice straw is supported by a measured plateau; the other three values are extrapolations beyond the concentration range studied and should be read as upper

estimates. These capacities are of the same order as those of recently reported thermally converted sorbents from the same feedstocks, and identify low-temperature phosphorylation of banana peel in particular as a candidate worth further characterisation, regeneration studies and testing on real effluents.

References

- [1] H. Babich, M. A. Devanas, and G. Stotzky, "The mediation of mutagenicity and clastogenicity of heavy metals by physicochemical factors," *Environ. Res.*, vol. 37, pp. 253–286, 1985.
- [2] C. Zamora-Ledezma et al., "Heavy metal water pollution: A fresh look about hazards, novel and conventional remediation methods," *Environ. Technol. Innov.*, vol. 22, art. no. 101504, 2021, doi: 10.1016/j.eti.2021.101504.
- [3] N. A. A. Qasem, R. H. Mohammed, and D. U. Lawal, "Removal of heavy metal ions from wastewater: A comprehensive and critical review," *npj Clean Water*, vol. 4, art. no. 36, 2021, doi: 10.1038/s41545-021-00127-0.
- [4] F. Fu and Q. Wang, "Removal of heavy metal ions from wastewaters: A review," *J. Environ. Manage.*, vol. 92, pp. 407–418, 2011.
- [5] R. Vidu, E. Matei, A. M. Predescu, B. Alhalaili, C. Pantilimon, C. Tarcea, and C. Predescu, "Removal of heavy metals from wastewaters: A challenge from current treatment methods to nanotechnology applications," *Toxics*, vol. 8, art. no. 101, 2020, doi: 10.3390/toxics8040101.
- [6] N. Feng, X. Guo, S. Liang, Y. Zhu, and J. Liu, "Biosorption of heavy metals from aqueous solutions by chemically modified orange peel," *J. Hazard. Mater.*, vol. 185, pp. 49–54, 2011.
- [7] Y. C. Lee and S. P. Chang, "The biosorption of heavy metals from aqueous solution by *Spirogyra* and *Cladophora* filamentous macroalgae," *Bioresour. Technol.*, vol. 102, pp. 5297–5304, 2011.
- [8] M. Inyang, B. Gao, Y. Yao, Y. Xue, A. R. Zimmerman, P. Pullammanappallil, and X. Cao, "Removal of heavy metals from aqueous solution by biochars derived from anaerobically digested biomass," *Bioresour. Technol.*, vol. 110, pp. 50–56, 2012.
- [9] M. Kılıç, Ç. Kırbıyık, Ö. Çepelioğullar, and A. E. Pütün, "Adsorption of heavy metal ions from aqueous solutions by bio-char, a by-product of pyrolysis," *Appl. Surf. Sci.*, vol. 283, pp. 856–862, 2013.
- [10] F. M. Pelleria, A. Giannis, D. Kalderis, K. Anastasiadou, R. Stegmann, J. Y. Wang, and E. Gidarakos, "Adsorption of Cu(II) ions from aqueous solutions on biochars prepared from agricultural by-products," *J. Environ. Manage.*, vol. 96, pp. 35–42, 2012.
- [11] A. Witek-Krowiak, R. G. Szafran, and S. Modelski, "Biosorption of heavy metals from aqueous solutions onto peanut shell as a low-cost biosorbent," *Desalination*, vol. 265, pp. 126–134, 2011.
- [12] P. Y. Deng, W. Liu, B. Q. Zeng, Y. K. Qiu, and L. S. Li, "Sorption of heavy metals from aqueous solution by

- dehydrated powders of aquatic plants," *Int. J. Environ. Sci. Technol.*, vol. 10, pp. 559–566, 2013.
- [13] L. T. Hung, P. T. Quan, L. M. Tam, and N. X. Thom, "Study on the adsorption and ion exchange capacity of modified coconut coir and rice husk," *Science and Technology Development Journal* (in Vietnamese), vol. 11, no. 08, 2008.
- [14] S. R. Shukla, R. S. Pai, and A. D. Shendarkar, "Adsorption of Ni(II), Zn(II) and Fe(II) on modified coir fibres," *Sep. Purif. Technol.*, vol. 47, pp. 141–147, 2006.
- [15] S. Gupta, S. Sireesha, I. Sreedhar, C. M. Patel, and K. L. Anitha, "Latest trends in heavy metal removal from wastewater by biochar based sorbents," *J. Water Process Eng.*, vol. 38, art. no. 101561, 2020, doi: 10.1016/j.jwpe.2020.101561.
- [16] F. O. Afolabi, P. Musonge, and B. F. Bakare, "Bio-sorption of copper and lead ions in single and binary systems onto banana peels," *Cogent Eng.*, vol. 8, no. 1, art. no. 1886730, 2021, doi: 10.1080/23311916.2021.1886730.
- [17] X. Wang, X. Wang, W. Chen, J. Yuan, and Q. Zhang, "Adsorption of Cu(II) and Pb(II) in aqueous solution by biochar composites," *ACS Omega*, vol. 10, no. 14, pp. 13816–13828, 2025, doi: 10.1021/acsomega.4c06837.
- [18] S. Mishra, A. K. Mohanty, L. T. Drzal, M. Misra, S. Parija, S. K. Nayak, and S. S. Tripathy, "Studies on mechanical performance of biofibre/glass reinforced polyester hybrid composites," *Compos. Sci. Technol.*, vol. 63, no. 10, pp. 1377–1385, Aug. 2003, doi: 10.1016/S0266-3538(03)00084-8.
- [19] R. M. Rowell, R. A. Young, and J. K. Rowell, *Paper and Composites from Agro-Based Resources*. Boca Raton, FL, USA: CRC Lewis Publishers, 1997.
- [20] R. Gong, Y. Jin, J. Chen, Y. Hu, and J. Sun, "Removal of basic dyes from aqueous solution by sorption on phosphoric acid modified rice straw," *Dyes Pigm.*, vol. 73, pp. 332–337, 2007.
- [21] F. Wang, X. Hu, C. Tang, C. Liu, and Z. Zhu, "Phosphate-functionalized ramie stalk adsorbent for efficient removal of Zn²⁺ from water: Adsorption performance, mechanism, and fixed-bed column treatment of real wastewater," *Environ. Sci. Pollut. Res.*, vol. 30, no. 3, pp. 6245–6261, 2023, doi: 10.1007/s11356-022-22590-z.
- [22] T. Bai, Y. Yao, J. Zhao, L. Tian, and L. Zhang, "Adsorption performance and mechanism of H₃PO₄-modified banana peel hydrothermal carbon on Pb(II)," *Separations*, vol. 11, no. 1, art. no. 17, 2024, doi: 10.3390/separations11010017.
- [23] I. Langmuir, "The constitution and fundamental properties of solids and liquids. Part I. Solids," *J. Am. Chem. Soc.*, vol. 38, pp. 2221–2295, 1916.
- [24] H. M. F. Freundlich, "Über die Adsorption in Lösungen," *Z. Phys. Chem.*, vol. 57A, pp. 385–470, 1906.
- [25] J. Anwar, U. Shafique, W. U. Zaman, M. Salman, A. Dar, and S. Anwar, "Removal of Pb(II) and Cd(II) from water by adsorption on peels of banana," *Bioresour. Technol.*, vol. 101, pp. 1752–1755, 2010, doi: 10.1016/j.biortech.2009.10.021.
- [26] M. A. Al-Ghouti and D. A. Da'ana, "Guidelines for the use and interpretation of adsorption isotherm models: A review," *J. Hazard. Mater.*, vol. 393, art. no. 122383, 2020, doi: 10.1016/j.jhazmat.2020.122383.
- [27] J. Wang and X. Guo, "Adsorption isotherm models: Classification, physical meaning, application and solving method," *Chemosphere*, vol. 258, art. no. 127279, 2020.