

## ADSORPTION OF Cu(II), Cd(II), AND Pb(II) USING A NOVEL ADSORBENT BASED ON POLYVINYL ALCOHOL ANCHORING CITRIC ACID (PVA-CA)

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### ABSTRACT

Heavy metals are widely used in industry. On the other hand, heavy metals cause environmental pollution. One technique for removing heavy metals is adsorption. By reacting polyvinyl alcohol with triethyl citrate, a novel adsorbent based on polyvinyl alcohol attaching citric acid (PVA-CA) has been successfully formed, as shown by FTIR spectra. The adsorption test was carried out under acidic conditions for metal ions, namely Cu(II), Cd(II), and Pb(II). Experimental results on metal ions Cu(II), Cd(II), and Pb(II) obtained that the optimum pH for the adsorption of each metal were 4.64, 3.92, and 4.65, respectively. The adsorption mechanism was ion exchange and was supported by coordination bonds between metal ions and C=O oxygen atom of carboxylic group; the slope value and FTIR measurements confirmed this. SEM-EDX was used to confirm the morphology of the adsorbent and metals adsorbed on the PVA-CA surface. The maximum loading capacity of Cd(II) was higher than Pb(II) and Cu(II), for each metal were 1.33, 0.69, and 0.67 mol/ kg for Cu(II), Cd(II), and Pb(II), respectively. From the capacity value, which was relatively high compared to other adsorbents, PVA-CA has excellent potential as an adsorbent to overcome environmental pollution problems caused by heavy metals such as Cu(II), Cd(II), and Pb(II).

**Keywords:** New adsorbent, Adsorption, Polyvinyl Alcohol-Citric Acid (PVA-CA), Cu(II), Cd(II), Pb(II).

### 1. Introduction

Heavy metal pollution is currently one of the severe environmental problems faced by the world community, especially in developing countries. Its sources not only form naturally but also come from industrial waste. Heavy metal are toxic, tend to accumulate in living bodies, possibly carcinogenicity, non-degraded chemically or biologically, biomagnified in the food chain, and poisonous even at low concentrations. (Darban et al., 2022; Gurgel et al., 2008; Ling et al., 2017; Nriagu J.O. & Pacyna J., 1988). Furthermore, heavy metals such as cadmium (Cd), lead (Pb), and copper (Cu) cause serious health problems, even death. In particular, Cd(II) with an estimated lethal oral dose for humans is 350-3500 mg (WHO, 2011). Pb(II) in the blood (PbB) with a concentration of  $\leq 5$   $\mu\text{g/dL}$  has a severe effect (e.g., neurological, renal, cardiovascular, hematological, immunological, reproductive, and developmental effects) (Abadin et al., 2020). For copper although humans need a certain amount of copper as a micronutrient for growth, excessive intake of copper can cause poisoning (National Research Council, 1995; Services, 2004).

Several techniques for removing heavy metals have been widely used in the past decade, such as ultrafiltration (Cao et al., 2020; Trivunac & Stevanovic, 2006; Y. Wang et al., 2022), chemical precipitation (Chen et al., 2018; X. Yang et al., 2023), evaporation (Kumar et al., 2023), solvent extraction (Djedidi et al., 2009), ion exchange (Chauhan et al., 2022; Tavakoli et al., 2017), and adsorption (Chakraborty et al., 2022; Darban et al., 2022; J.-S. Yang et al., 2010). Among these techniques, adsorption is the most promising and attractive because of its affordable cost, relatively simple techniques, and relatively high efficiency and availability of various adsorbents.

In recent years, many researchers have been developing polymer-based adsorbents because of attractive characteristics that are chemical and physical stability, resistance to heat, and extreme environmental conditions. Additionally, due to their functionalization, polymeric

adsorbents also have excellent adsorption capacity for removing various heavy metals with various characteristics (Chua et al., 2021; Zaimie et al., 2021).

Liu et al., 2023 (C. Liu et al., 2023) reported their study using a 2-hydroxypropyl- $\beta$ -cyclodextrin (HPCD) polymer functionalized with citric acid (CA) to remove the cationic dye-methylene blue (MB) from water with the maximum theoretical absorption capacity of HPCD-CA 0.25 for MB is  $1.556 \text{ mol kg}^{-1}$ , while Liu et al. 2018 (X. Liu et al., 2018) with the same functionalization by anchoring it in three types of resin, namely PS-Cl, PS-OH, and PS-NH<sub>2</sub> which are used to adsorb Hg(II), Al(III), Cu(II), Pb(II), Cd(II), and Fe(III) with the results of the combination of PS-NCA was a promising adsorbent to Hg(II) and Al(III) with maximum loading capacity values of  $0.573 \text{ mol kg}^{-1}$  and  $6.546 \text{ mol kg}^{-1}$ , respectively and the PS-CA combination was a good adsorbent to Cu(II), Pb(II), and Cd(II), and Fe(III) with maximum loading capacity values of  $1.218 \text{ mol kg}^{-1}$ ,  $0.091 \text{ mol kg}^{-1}$  and  $1.066 \text{ mol kg}^{-1}$ , and  $2.577 \text{ mol kg}^{-1}$ , respectively as well as other researchers who investigated polymeric adsorbent that functionalized citric acid as an active group in adsorption to remove various heavy metals.

One of the polymers is polyvinyl alcohol (PVA), which has the advantages of compatibility, low cost, biodegradability, and lots of OH groups, allowing cross-linking effects formation (Abdeen et al., 2015; L. Y. Wang & Wang, 2016). However, PVA is still widely researched and developed as a polymer-based material in the form of hydrogels and membranes, and there is very limited literature that makes it an adsorbent, and there is no research on PVA-CA as an adsorbent. By anchoring CA as a functional group, a tripodal compound with three carboxylic acid groups is expected to bind metal ions of a specific size.

In this study, we have prepared a novel adsorbent from polyvinyl alcohol embedded with citric acid (PVA-CA) for adsorbing of Cu(II), Cd(II), and Pb(II) metal ions. The influence of experimental parameters such as pH, contact time, and maximum loading capacity was analyzed and discussed. The adsorption mechanisms were also included. Furthermore, metal adsorption in competitive systems and elution processes was reported.

## 2. Material and Methods

### 2.1 Chemical

H<sub>2</sub>SO<sub>4</sub>, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O was purchased from Wako Pure Chemical Industries, Ltd., Osaka, Japan. All other chemicals were of analytical grade and were used without further purification. Metals stock solutions were prepared by dissolving amounts of Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O in 0.1 M (M = mol dm<sup>-3</sup>) of HCl and 0.1 M HEPES to adjust pH.

### 2.2 Preparation of PVA-CA adsorbent

PVA-CA adsorbent was prepared by dissolving 1.13 g of PVA with 40 mL of distilled water under heating. After the PVA dissolved, the solution was cooled, and 1 mL of 4 M sulfuric acid was added. Triethyl citrate is added as much as 13.12 g into it. The mixture was heated at 130 °C until the solvent evaporated and obtained a solid black product. For an appropriate and consistent size, the solid was crushed.

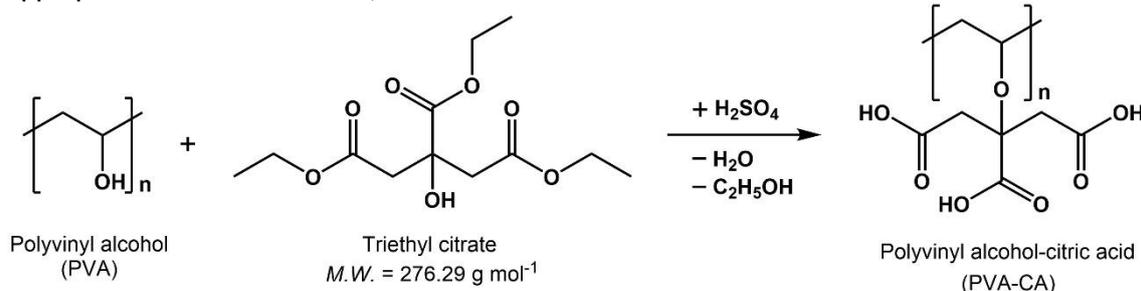


Fig. 1. Schematic preparation of PVA-CA adsorbent.

### 2.3 Characterization of PVA-CA

The Fourier Transform Infrared Spectroscopy (FT-IR) by Merck JASCO FT/IR-410 (JASCO Corp., Tokyo, Japan) was preferably done to ensure and identify characteristic functional groups of the desired compound or PVA-CA. When the adsorbent adsorbs metal ions, FTIR measurements may occasionally detect a wavelength change in the adsorbent or intensity. Using the KBr pellet method for sample handling, the spectra were recorded from 4000 to 500  $\text{cm}^{-1}$ . Imaging and determining the metals was adsorbed analysis was conducted by scanning electron microscopy - energy dispersive X-ray (SEM-EDX) Hitachi, SU8000, Tokyo, Japan. The metal ion concentration in the solution was measured by using a Shimadzu model ICPS-8100 inductively coupled plasma atomic spectrometer (ICP-AES) from Shimadzu Corp., Kyoto, Japan.

#### 2.3.1 Adsorption Experiment

0.1 mM solution of Cu(II), Cd(II), and Pb(II) was prepared by diluting from a stock solution in 0.1 M of HCl and 0,1 M HEPES to adjust pH. pH was adjusted 1–6 and measured using a pH meter. Ten milligram adsorbent was added in sample vials with 10 mL of 0.1 mM metal solution. Adsorption tests were carried out batch-wise to observe the adsorption behavior of various metal ions on the tested from individual metal solutions. A thermostat incubator of THOMAS AT24R was used for shaking at 30 °C for 24 and 48 hours Cu(II), Cd(II), and Pb(II) to reach equilibrium. The percentage of adsorption was calculated according to the Eq.1

$$\%Ads = \frac{C_i - C_e}{C_i} \times 100 \quad (1)$$

where  $C_i$  and  $C_e$  are the initial and equilibrium concentrations of tested metal ion (mM), respectively, the amount of metal adsorbed on the adsorbent ( $q$ ) was calculated according to the Eq.2.

$$q = \frac{C_i - C_e}{M} \times V \quad (2)$$

where  $V$  is the volume of the test solution (L), and  $M$  is the dry weight of the adsorbent (kg).

Adsorption isotherm tests were carried out by shaking 10 mg of adsorbent and 10 mL of metal solutions with various concentrations.

Desorption was done by shaking the adsorbent that had absorbed the metal with 10 mL of hydrochloric acid (HCl) and nitric acid ( $\text{HNO}_3$ ) eluent with various concentrations. The time and temperature used were the same as the adsorption conditions. After shaking, filtration was carried out. The filtrate solution was then measured using ICP-AES. The percentage of desorption was calculated according to the Eq.3, where  $C_{el}$  was the elution concentration of tested metal ion (mM).

$$\%El = \frac{C_{el}}{C_i - C_e} \times 100 \quad (3)$$

To determine the exchangeable ion of PVA-CA used titration method. The stoichiometry can be estimated by Eq. 4.

$$\text{Stoichiometry} = \frac{\text{amount of loaded metal ion (mmol)}}{\text{amount of protonated of polymelamine (mmol)}} \quad (4)$$

## 3. Results and Discussions

### 3.1. FT-IR analysis

Fig. 2.a shows the results of the of PVA and PVA-CA FT-IR spectra. On the PVA spectrum (black line), absorption was seen in the area around 3300 to 3500  $\text{cm}^{-1}$ , which shows

the OH group. Whereas in the PVA-CA spectrum (red line), new peaks appear in the wavelength region of  $1735\text{ cm}^{-1}$  and  $1197\text{ cm}^{-1}$ , which belong to the C=O (carboxylic) and C-O (carboxylic, alcohols, esters, and ethers) groups, respectively. However, the C-O group does not come from esters because there are no other peaks around  $1100$  to  $1030\text{ cm}^{-1}$  belonging to O-C-C, as Smith (2002) (Smith, 2022) explained regarding the rule of three peak positions for saturated esters. The region of about  $2500$ – $3500\text{ cm}^{-1}$  is ascribed to overlapping broad bands of the -OH of the carboxylic acid and the polyvinyl alcohol. Generally, the FT-IR results, the PVA-CA adsorbent, was successfully synthesized.

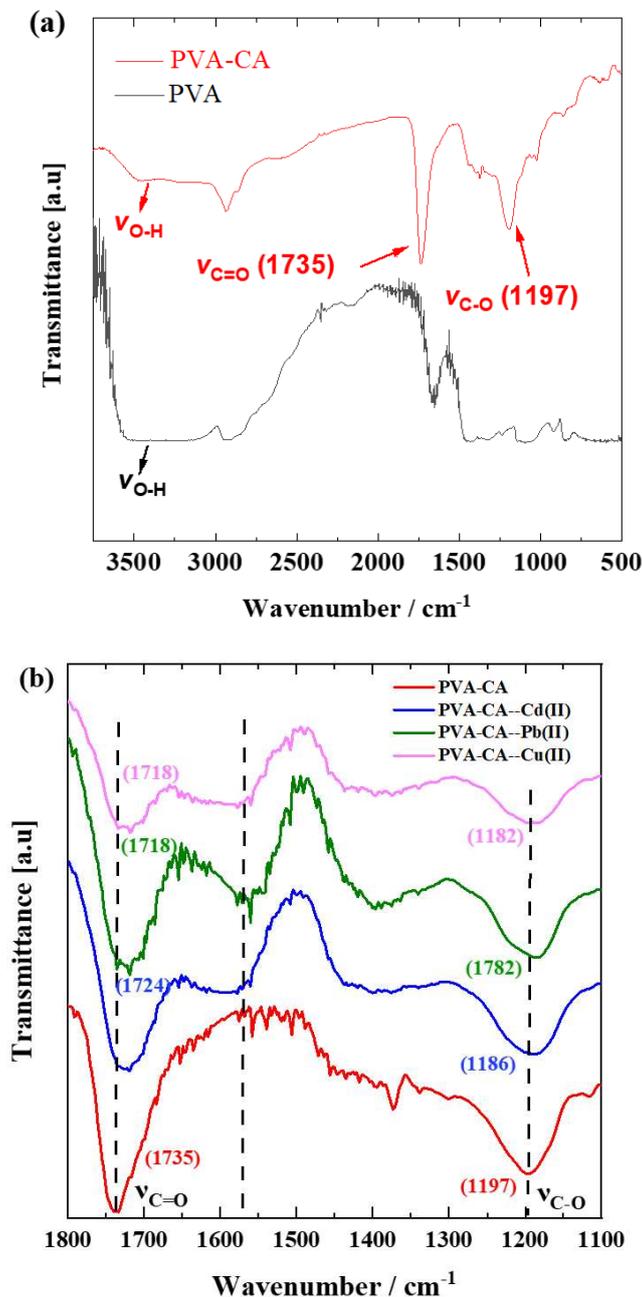


Fig. 2. (a) PVA and PVA-CA, (b) PVA-CA before and after adsorption of Cu(II), Cd(II), and Pb(II) on the PVA-CA.  $[\text{Cu(II)}], [\text{Cd(II)}], [\text{Pb(II)}] = 1\text{ mM}$ , adsorbent = 0.01 g.

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### 3.2. Time course dependency

The effect of contact time of Cu(II), Cd(II), and Pb(II) on the adsorption percentage of the PVA-CA adsorbent is shown in Fig. 3. The curve shows that the percentage of adsorption increases with increasing time. The adsorption rate in the initial phase in the first 8 h due to the opened active adsorbent site, which resulted in metal ions interacting with the surface of the

adsorbent easily. Additionally, the concentration difference between the solid-liquid interface and the solution was high initially, so the driving force for adsorption becomes stronger. Then, after the initial phase, the adsorption rate slightly increases until it reaches equilibrium. This slower adsorption rate than the initial phase was due to the slower metal diffusion into the adsorbent (B. Zhu et al., 2008). In this figure, it was also seen that it takes 48, 24, and 24 hours to reach an equilibrium state for Cu(II), Cd(II), and Pb(II), respectively.

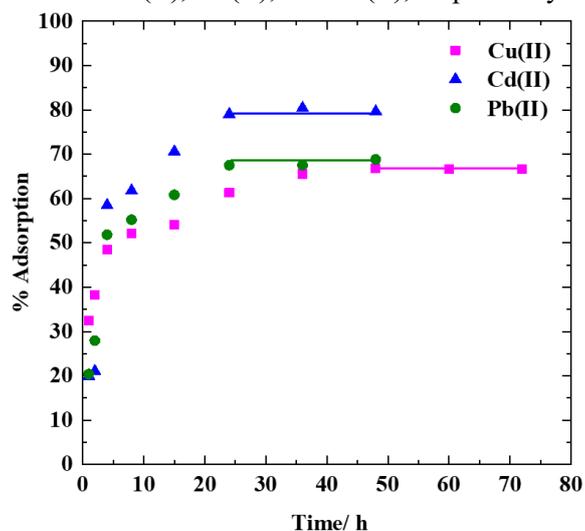


Fig. 3. Effect of contact time of Cu(II), Cd(II), and Pb(II) on the PVA- CA. [Cu(II)], [Cd(II)], [Pb(II)] = 0.1 mM, adsorbent = 0.01 g. Vol = 10 mL

### 3.3. pH dependency.

The pH of aqueous solutions influences adsorption at the solid-liquid interface significantly. Because pH impacts the solubility of metal ions and the concentration of counter ions in the functional groups of the adsorbent (Atieh et al., 2010).

Fig. 4 illustrates the effect of pH on the adsorption of Cu(II), Cd(II), and Pb(II) ions on the surface of the PVA-CA adsorbent. The percentage of adsorption is relatively low, below pH 3 for the three metals, due to competition between H<sup>+</sup> and metal ions on the active site of the adsorbent. Other researchers also presented the same analysis (Abdeen et al., 2015; Hassan et al., 2021; Liang et al., 2020). On the other hand, at pH above 3, the adsorption percentage increased significantly due to the -COOH group dissociating negatively charged (-COO<sup>-</sup>). Consequently, the more negative charge on the surface of the adsorbent, the more metal ion adsorbed (S. Wang et al., 2019). Adsorption behavior in which the percentage of adsorption increases with increasing pH indicates an ion exchange mechanism (Inoue et al., 2015).

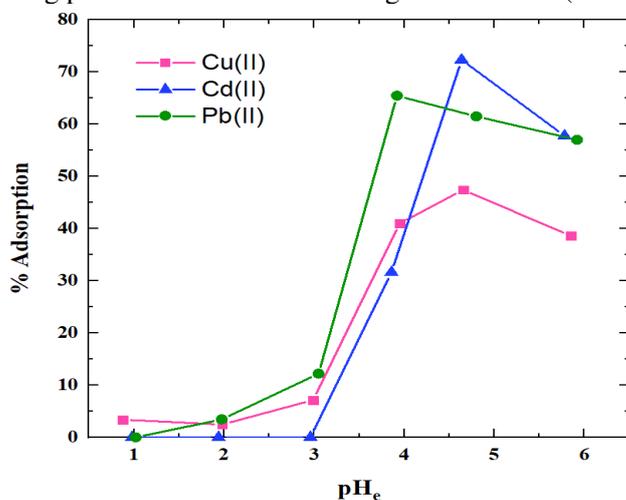


Fig. 4. Effect of pH for adsorption of Cu(II), Cd(II), and Pb(II) onto the PVA-CA. [Cu(II)], [Cd(II)], [Pb(II)] = 0.1 mM, adsorbent = 0.01 g. Vol = 10 mL

**Fig. 4** also shows the pH that gives the maximum adsorption percentage. The maximum adsorption for each metal was found at pH 4.64, 4.65, and 3.92 for Cu(II), Cd(II), and Pb(II), respectively. Upon reaching that pH, the adsorption percentage slightly decreased due to hydrolysis of metal ions.

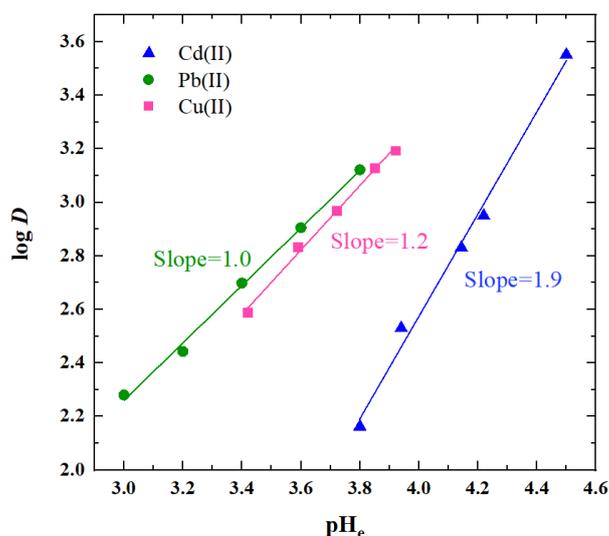


Fig. 5. Slope of metals in adsorption process. [Cd(II)], [Pb(II)], [Cu(II)] = 0.1 mM, adsorbent = 0.02 g. Vol = 10 mL

**Fig. 5** is a graph of the relation between equilibrium pH (pH<sub>e</sub>) and log *D* that describes the slope of metal ions in the adsorption process. *D* was calculated using Eq.5 where *q<sub>e</sub>* and *C<sub>e</sub>* were the the amount of metal adsorbed on the adsorbent and concentration in equilibrium state respectively.

$$D = \frac{q_e}{C_e} \tag{5}$$

The slope is related to the ion exchange mechanism that indicates the amount of H<sup>+</sup> released from the adsorbent to the solution. The figure shows that Cu(II), Cd(II), and Pb(II) have a slope of 2, 1, and 1, respectively. Additionally, with the release of H<sup>+</sup> into the solution, the pH at the equilibrium state is lower than the initial pH.

### 3.4. Adsorption isotherm

In this study, the Langmuir model (Langmuir, 1916) was used to determine isothermal adsorption for Cu(II), Cd(II), and Pb(II) to PVA-CA by the Eq.6:

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \tag{6}$$

The linier form of Langmuir model is defined by the Eq.7:

$$\frac{C_e}{q_e} = \left( \frac{1}{q_{max} \times K_L} \right) + \left( \frac{q_e}{q_{max}} \right) \tag{7}$$

Where *q<sub>e</sub>* and *q<sub>max</sub>* are the amount of metal at equilibrium and the maximum amount of metal ions adsorbed at equilibrium (mol kg<sup>-1</sup>), respectively, *C<sub>e</sub>* is the equilibrium concentration of metal ions in the aqueous phase (mol L<sup>-1</sup>), and *K<sub>L</sub>* is Langmuir adsorption constant (L mol<sup>-1</sup>).

**Fig. 6** shows that Langmuir adsorption type, where adsorption increases with increasing initial concentration of metal ions until adsorption reaches a maximum value for each metal. The model describes the formation of a homogeneous monolayer on the surface of the adsorbent. By using Eq.7 the maximum capacities of Cd(II), Cu(II), and Pb(II) are 1.33, 0.67, and 0.69 mol kg<sup>-1</sup> respectively.

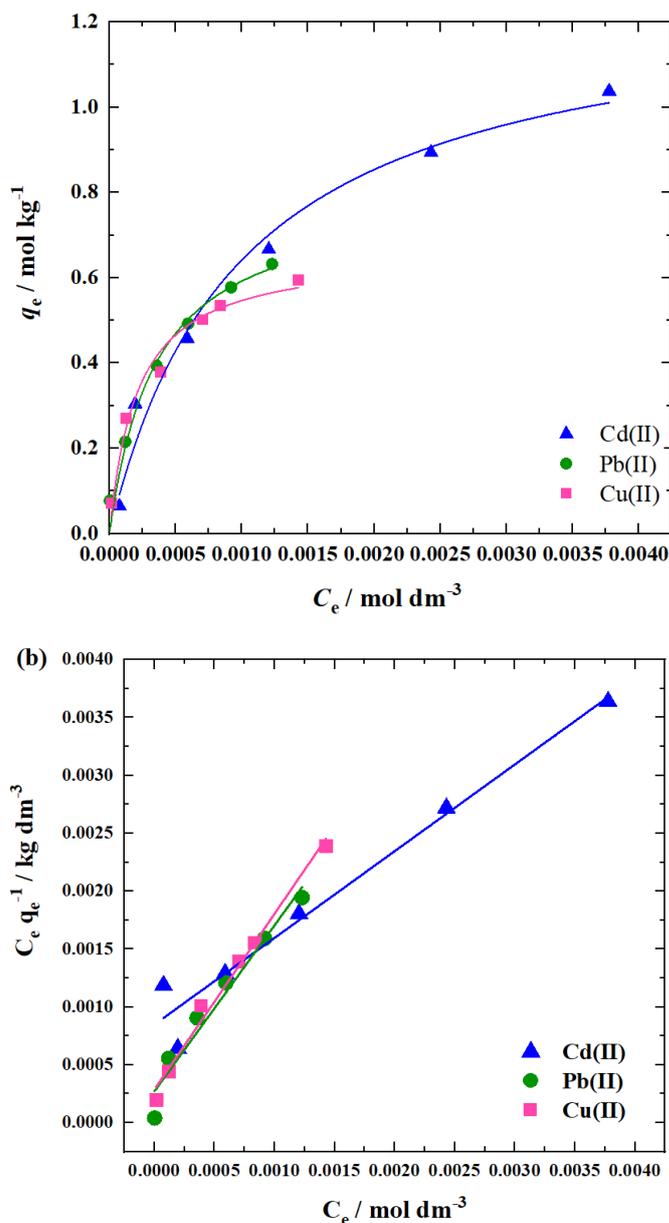


Fig. 6. Langmuir adsorption isotherm of Cd(II), Pb(II) and Cu(II) onto the PVA-CA. [Cd(II)], [Pb(II)], [Cu(II)] = 1 mM, adsorbent = 0.01 g, Vol = 10 mL.

The maximum loading capacity for cadmium metal is relatively high. The comparison of the maximum capacity of Cd(II) metal against several adsorbents with PVA-CA is shown in **Table 1**.

Table 1 - Maximum capacity of Cd(II) metal towards several adsorbents

Adsorbent	Adsorption Capacity in mg g <sup>-1</sup> or mol kg <sup>-1</sup>	Reference
Porous attapulgitite (ATP)/polymer beads	32.7 // 0.29	(Feng et al., 2017)
mGO/SiO <sub>2</sub> /PPy-co-Th	80 // 0.71	(Molaei et al., 2017)
Picea smithiana sawdust	2.87 // 0.026	(Mahmood-Ul-Hassan et al., 2018)
Cd <sup>2+</sup> -ion-imprinted polymer (Cd <sup>2+</sup> -IIP) with thiol-functionalized polymer	35.25 // 0.56	(Kong et al., 2018)
SG-G2.0	35.97 // 0.32	(Y. Zhu et al., 2018)
PANI/jute fiber composites	140 // 1.24	(Huang et al., 2019)

G-3PAMAMSGA	28.49 // 0.25	(Ebelegi et al., 2020)
modified cellulose nanofiber (CNFs)	45.9 // 0.41	(Movaghgharnezhad et al., 2020)
Halloysite nanotubes (HNT)-ball-milled	6.96 // 0.06	(Hassan et al., 2021)
biochar(BC)@Alg. POPd/CDs	36.20 // 0.32	(Meng et al., 2021)
60-MWCNTs@Fe <sub>3</sub> O <sub>4</sub>	57.3 // 0.51	(Z. Wang et al., 2021)
La-Fe incorporated chitosan beads (LaFe@CS)	35.5 // 0.32	(Lan et al., 2022)
Coal fly ash (CFA) and red mud (RM)	127.82 // 1.14	(Zhao et al., 2023)
Modified Fly Ash (MFA)	68.8 // 0.61	(Singh et al., 2023)
Cd(II)-IIPs	50.54 // 0.45	(Qi et al., 2023)
Cd(II)-IIP based on octavinyl polyhedral oligomeric silsesquioxane (OV-POSS)	80.21 // 0.71	(Ding et al., 2023)
Polyvinyl Alcohol-Citric Acid (PVA-CA)	149.5 // 1.33	This study

### 3.5 Adsorption of metal ions in competitive system

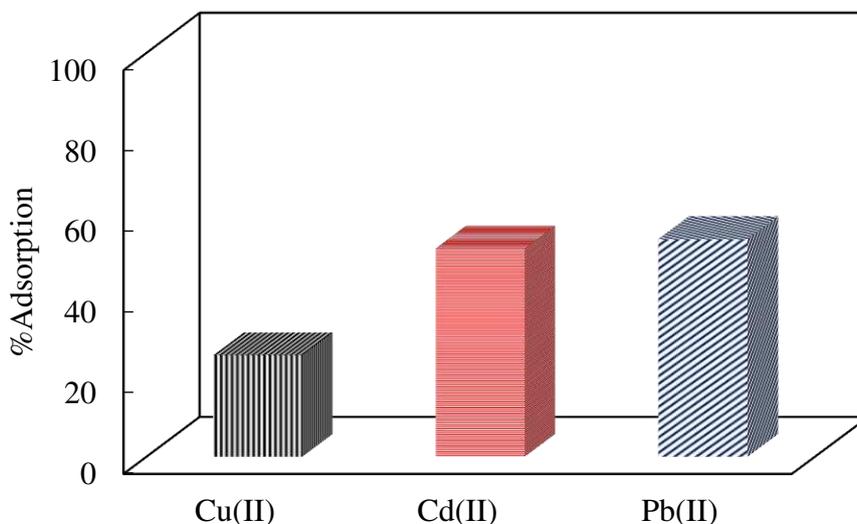


Fig. 7. Metals adsorption with PVA-CA in competitive system. [Cu(II)], [Cd(II)], [Pb(II)] = 0.1 mM, weight of PVA-CA = 0.01 g. Vol = 10 mL.

**Fig. 7** shows that the adsorption percentage of the three metals in competitive systems. The adsorption percentage is lower than the adsorption percentage of individual system. In the individual systems, the adsorption percentages for each metal are about 80, 70, and 60% for Cu(II), Cd(II), and Pb(II) respectively. However, in a competitive system, the adsorption percentage is about 50% for Cd(II) and Pb(II) and about 25% for Cu(II). The lower percentage of adsorption in this competition system is due to the presence of other metals which suppress the adsorption of metal ions on the surface of the adsorbent. From the figure it can also be seen that the PVA-CA adsorbent is not selective for the three metals in this adsorption condition.

### 3.6 Proposed adsorption mechanism

In adsorption, the slope shows the amount of H<sup>+</sup> released by the adsorbent into the solution. In this process, there is an exchange of cations where metal ions replace the released H<sup>+</sup>. Based on the slope obtained in **Fig. 5** Cd(II) has slope of 2, Pb(II) and Cu(II) have slope of 1, which means that the adsorbent adsorbs Cd(II), releasing two H<sup>+</sup>, while adsorbents for adsorbing Pb(II) and Cu(II) release one H<sup>+</sup>. This mechanism is called the ion exchange mechanism.

FTIR spectroscopy is a helpful tool for understanding adsorption mechanisms. **Fig. 2b** depict the results of the FTIR spectra of PVA-CA before and after the adsorption of Cu(II), Cd(II), and Pb(II), where there is a shift in the C-O peak. As shown in the peak curves for C-O in PVA-CA at  $1197\text{ cm}^{-1}$ , shifted to PVA-CA-Cd(II), PVA-CA-Pb(II), and PVA-CA-Cu(II) at  $1186$ ,  $1182$ , and  $1182\text{ cm}^{-1}$  respectively. The shift indicates that the -H atom in the carboxylic group in the adsorbent is involved in adsorption.

On the other hand, the peaks indicating C=O vibrations in the  $1735\text{ cm}^{-1}$  region shifted towards lower wave numbers after adsorption, namely  $1724$ ,  $1718$ , and  $1718\text{ cm}^{-1}$  for Cu(II), Cd(II), and Pb(II), respectively. In addition, after adsorption, the -C=O peak is split indicating coordination between the -O atom on the carbonyl group and the metal ions.

Based on this evidence, it can be stated that the primary adsorption mechanism for Cd(II), Cu(II), and Pb(II) is ion exchange and is supported by a coordination bond between the metal ion and the lone pair of electrons on the oxygen atom in the -COOH.

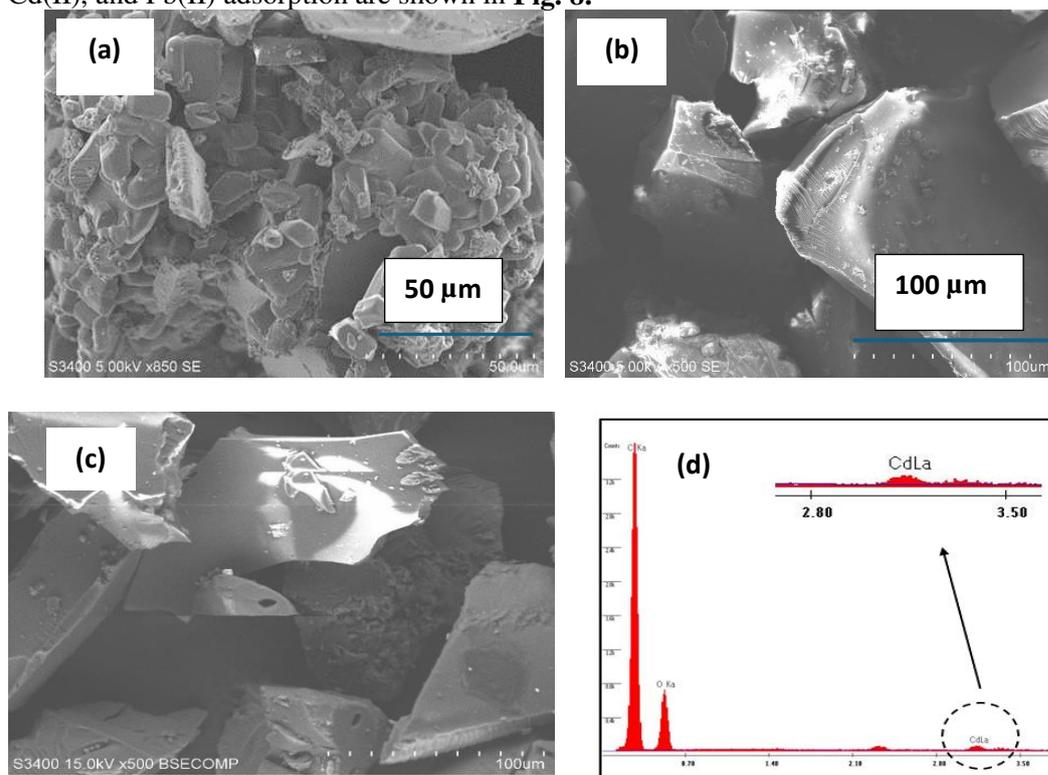
Table 2 - The maximum loading capacities for Cd(II), Cu(IV), and Pb(II) on PVA-CA and their stoichiometries.

Metal ion	Maximum loading capacity (mol $\text{kg}^{-1}$ )	Loading distribution ratio of metal ions (molecules of PVA-CA : metal ion)
Cd(II)	1.33	1.5 : 1
Cu(II)	0.67	3 : 1
Pb(II)	0.69	3 : 1

In addition, from Eq. 4, the ratios between PVA-CA and metals in the adsorption process were obtained as shown in Table 2 where the number of moles of ion exchangeable adsorbent was determined by titration, and the value was  $1.8\text{ mol kg}^{-1}$ . The estimated ratios obtained were 1.5 : 1 for Cd(II), and 3 : 1 for Cu(II) and Pb(II).

### 3.7. SEM EDX

The SEM micrographs and EDX spectra of synthesized PVA-CA before and after Cu(II), Cd(II), and Pb(II) adsorption are shown in **Fig. 8**.



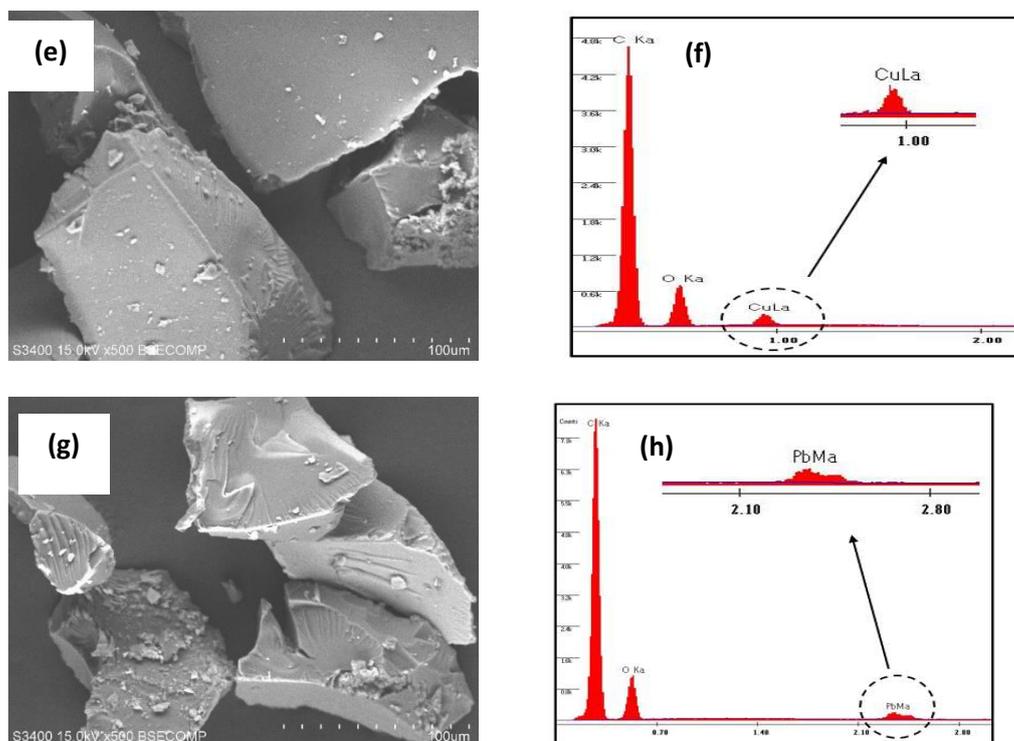


Fig. 8. SEM micrographs and EDS spectra of PVA-CA (a,b) before adsorption, (c,d) after adsorption Cd(II), (e,f) after adsorption Cu(II), (g,h) after adsorption Pb(II). [Cd(II)], [Pb(II)], [Cu(II)] = 1 mM, adsorbent = 0.01 g.

The PVA-CA SEM image in Figure 8 (a) shows, which is mostly rectangular with non-uniform size distributions before adsorption. The SEM image and EDX after adsorption of Cu(II), Cd(II), and Pb(II) are shown in **Fig. 8**(c, d), (e, f), and (g, h), respectively, where they were not significant visible changes in physical form before and after adsorption for all metal ions due to chemically bound to PVA-CA.

### 3.8 Elution

Desorption studies for all three metals have been carried out. **Fig. 9** shows the percentage of adsorption (left bar) and elution (right bar) for Cu(II), Cd(II), and Pb(II) metals. The eluent used were HCl with concentrations of 0.1, 1, and 2 M and HNO<sub>3</sub> with concentrations of 0.5 and 1 M. **Fig. 9a** indicated that Pb(II) metal and Cu(II) metal have almost the same elution percentage as percent adsorption for the three HCl concentrations used. However, the elution percentage of Cd(II) metal was shallow, below 10%. On the other hand, **Fig. 9b** shows that HNO<sub>3</sub> with the above concentration gives an elution percent of almost 100% of the adsorption percent for the three metals. When compared between the two eluents, HNO<sub>3</sub> was more effective than HCl for PVA-CA adsorbent.

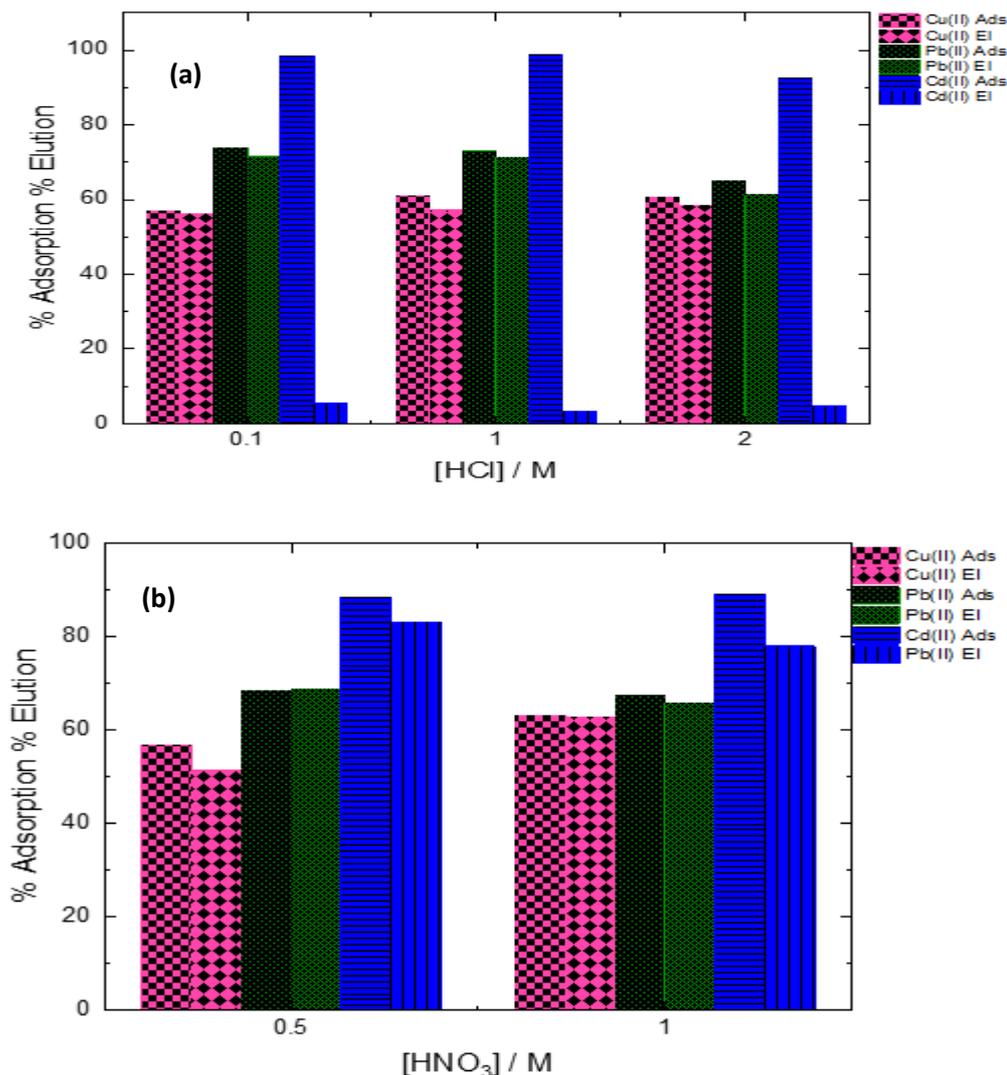


Fig. 9. Metal elution by using (a) HCl and (b) HNO<sub>3</sub> in different concentration. [Cd(II)], [Pb(II)] = 0.1 mM, weight of PVA-CA = 0.01 g. Vol = 10 mL.

#### 4. Conclusion

In this research, we have prepared a new polyvinyl alcohol (PVA-CA) based citric acid adsorbent. This adsorbent can adsorb Pb(II) and Cu(II) metals ion, 0.67 and 0.69 mol kg<sup>-1</sup>, respectively. Even cadmium metal was adsorbed with a maximum capacity of 1.33 mol kg<sup>-1</sup>. The metal adsorption mechanism was ion exchange and coordination bonds between the metal and the adsorbent. The slope and the FTIR analyses proved the mechanism. Based on these experimental results, the ability of the PVA-CA adsorbent to adsorb Pb(II), Cu(II), and especially Cd(II) were relatively high. Based on these results, we believe PVA-CA can be regarded as an adsorbent with significant potential for removing the metals Cu(II), Cd(II), and Pb(II) because of its relatively high capacity to adsorb Pb(II), Cu(II), and particularly Cd(II). Eluents for the desorption procedure have included HCl and HNO<sub>3</sub>. For these three metals, HNO<sub>3</sub> performs better than HCl.

**Declaration of Competing Interest:** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

**Credit authorship contribution statement:** **Reni Angraini:** Writing – original draft, Investigation, Data curation. **Shota Nakajima:** Investigation, Data curation. **Gehui Pang:** Data curation. **Shintaro Morisada:** Validation, Methodology. **Hidetaka Kawakita:** Validation,

Formal analysis. **Keisuke Ohto:** Writing – review & editing, Validation, Supervision, Methodology, Funding acquisition, Conceptualization.

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