



*54<sup>th</sup> Annual Meeting of The Clay Minerals Society*

# Co-Adsorption of Cd(II) and Phosphate on Hydroxyl-Aluminum (Al<sub>13</sub>) Montmorillonites

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# Introduction

## Heavy metal cations and phosphate pollution



Heavy metal pollution



Lake Eutrophication

- Inorganic ions
- Non-degradable



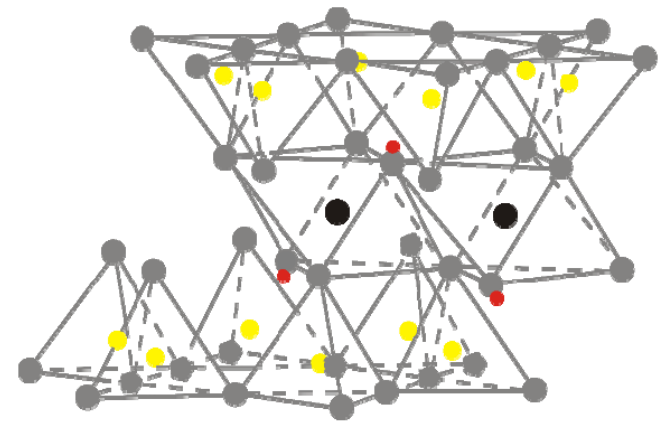
**Adsorption**

# Clay mineral based adsorbent

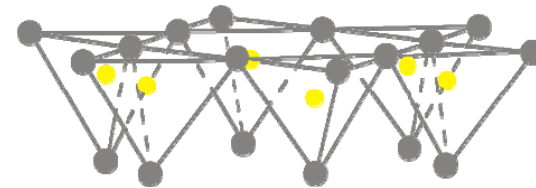
- ✓ Cheap
- ✓ Environmental friendly

## Montmorillonite

- High cation exchange capacity
- High specific surface area
- Hydrophilicity and swelling
- Structure and properties can be modified



Cations &  $n \cdot \text{H}_2\text{O}$



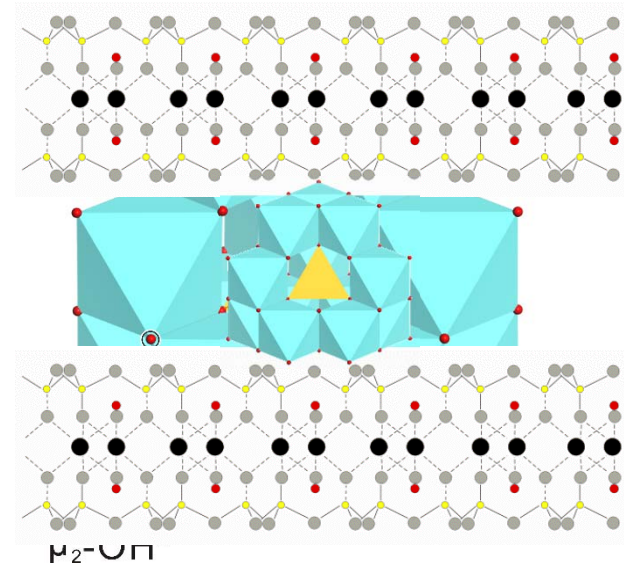
Structure of Montmorillonite  
(Grim, 1968)

# Hydroxyl-metal pillared montmorillonite

- Hydrolysis of metal (Al, Fe, La, etc)
- Cation exchange with original cations of Mt

## $\text{Al}_{13}$ cation

- High reactive surface hydroxyl group
- High specific surface area
- Strong affinity for both heavy metal cation and oxyanion (Schlegel, 2007; Yan et al., 2010)



$\text{Al}_{13}$  cation (Keggin structure)  
(Casey, 2006)

**the simultaneous adsorption of both contaminants**

# Simultaneous adsorption of heavy metal cations and oxyanions

## ➤ Decrease

formation of non-adsorbing cation-anion complex (Benjamin and Leckle, 1982)

competition for the same adsorption site (Li et al., 2013; )

## ➤ Increase (synergistic adsorption)

formation of ternary surface complex (Li et al., 2013; Elzinga and Kretzschmar, 2013)

surface precipitation (Talor et al., 2009)

## Hydroxyiron-Montmorillonite complex

Phosphate and Cd formed P-bridged ternary complexes (Zhu et al., 2014)

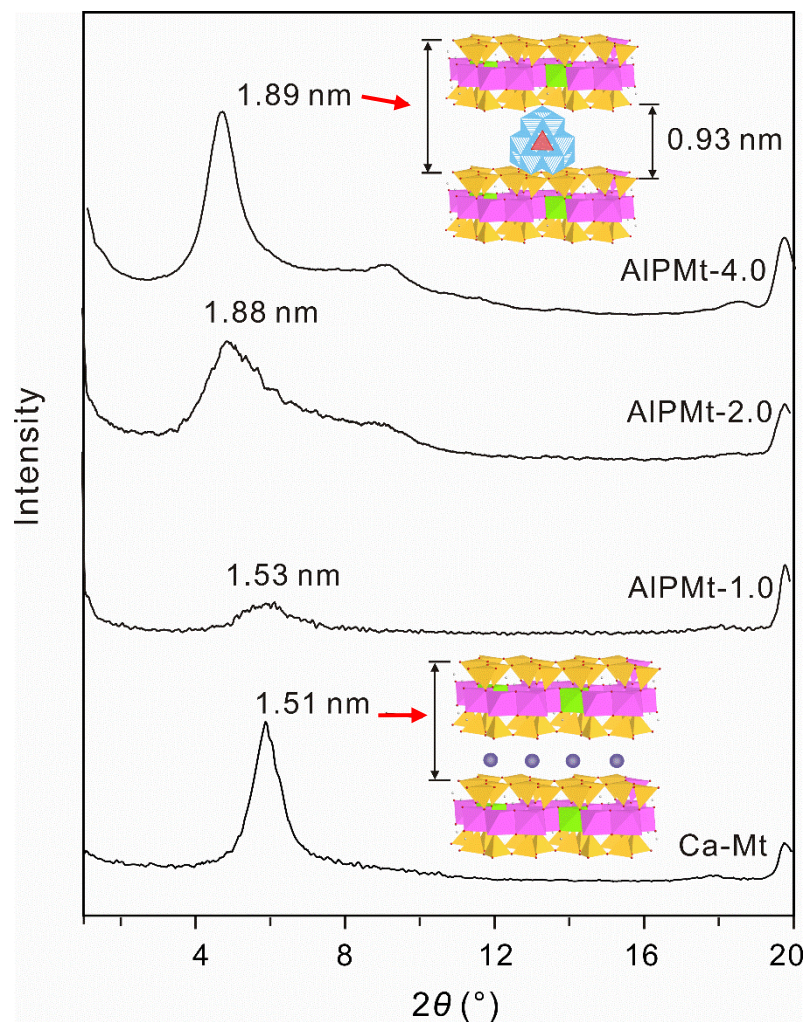
**$\text{Al}_{13}$  pillared montmorillonite?**

## **Simultaneous adsorption of phosphate and Cd<sup>2+</sup> on AlPMT**

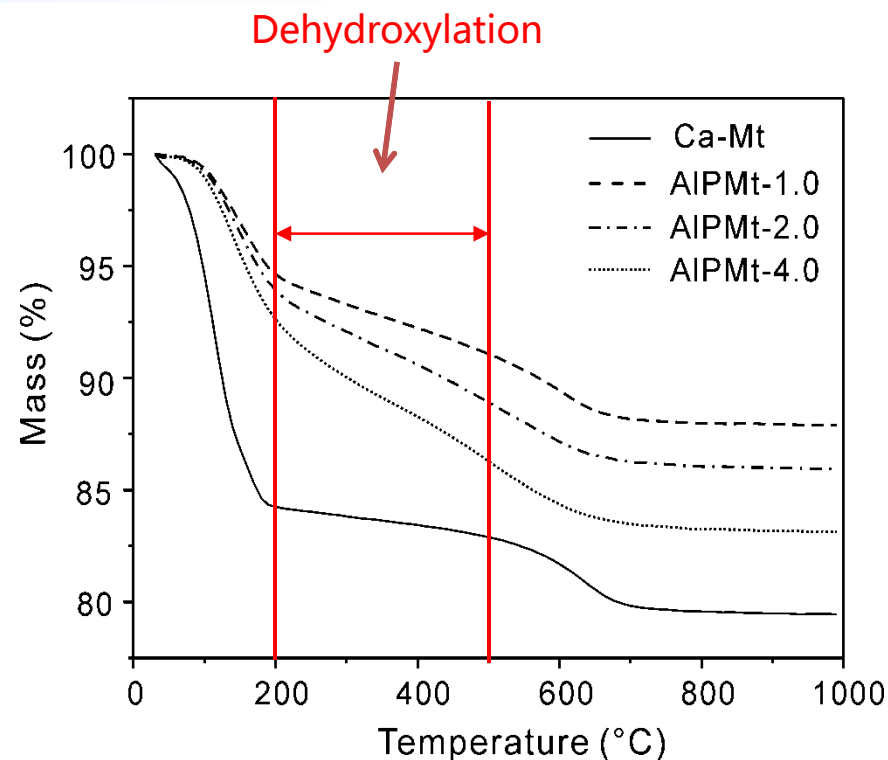
- **Effect of the structure and property**
- **Effect of the co-exist contaminant**



# Structure of $\text{Al}_{13}$ -montmorillonite



XRD patterns



TG curve

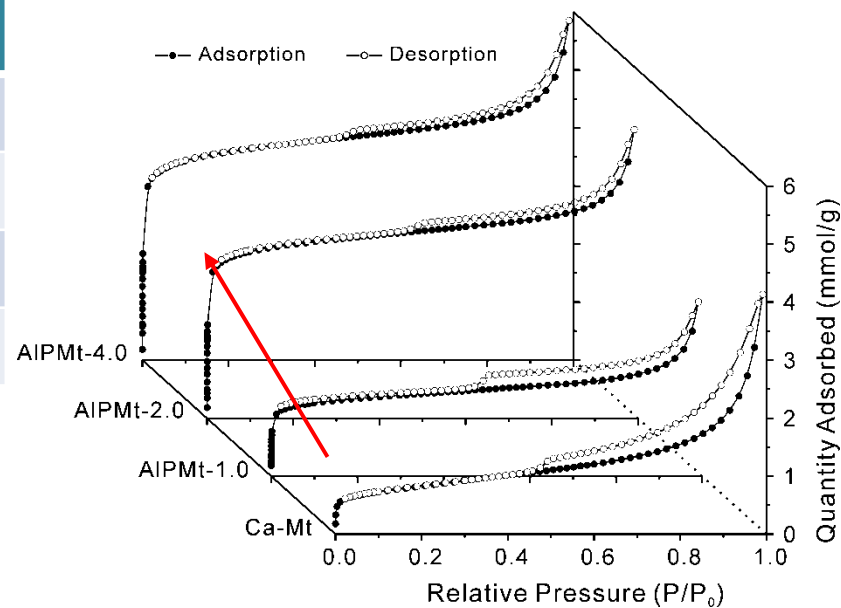
- Basal spacing
- $\text{Al}_{13}$  loaded



# Specific Surface Area

$Al_{13}$  contents and specific surface area

Samples	Mass Loss (200 – 500 °C, %)	BET (m <sup>2</sup> /g)
Ca-Mt	1.93	65.64
AIPMt-1.0	3.54	111.86
AIPMt-2.0	5.01	254.72
AIPMt-4.0	6.33	304.94



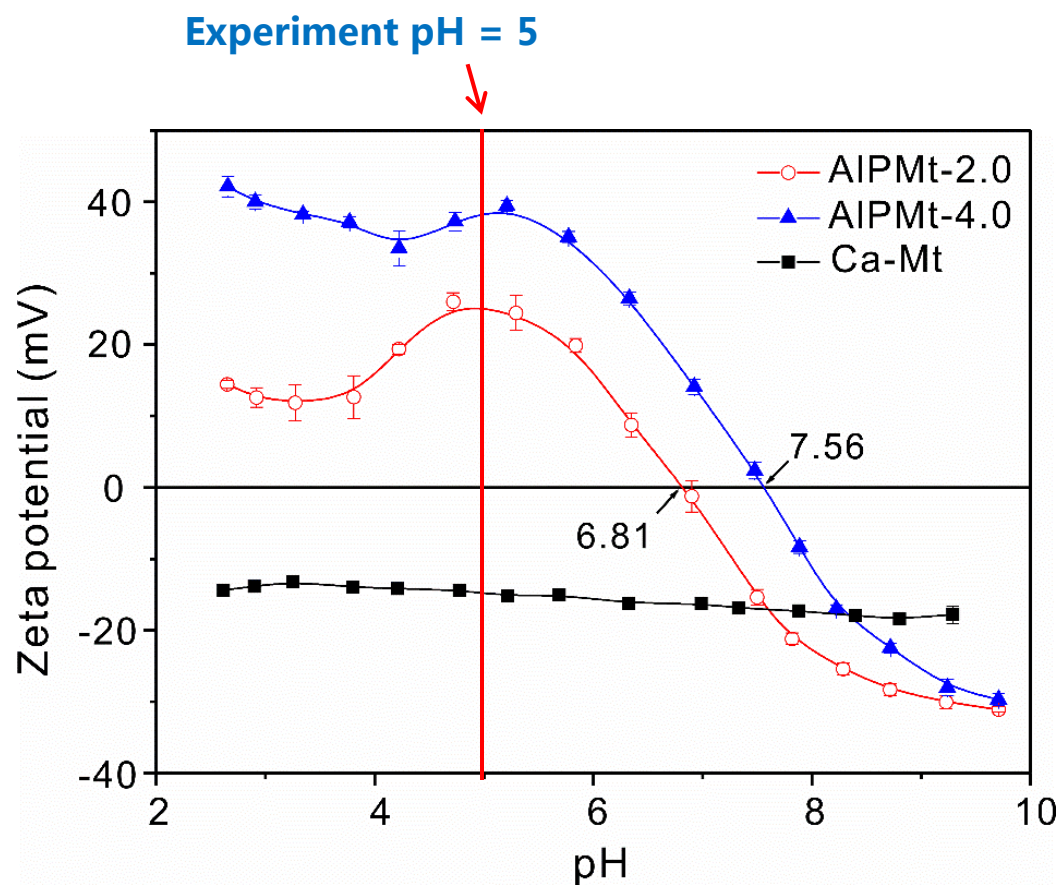
- Specific surface area
- Micropores



N<sub>2</sub> adsorption-desorption isotherms

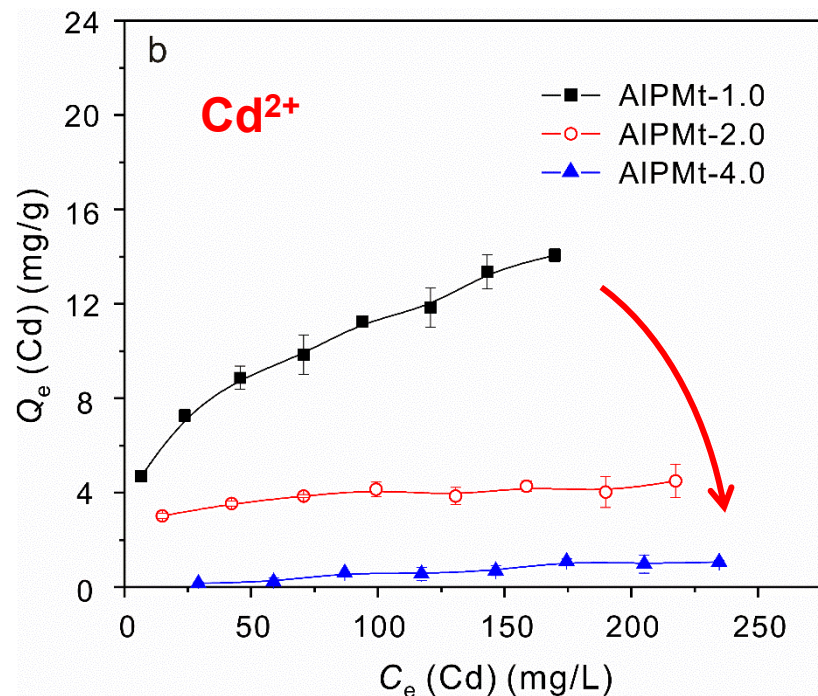
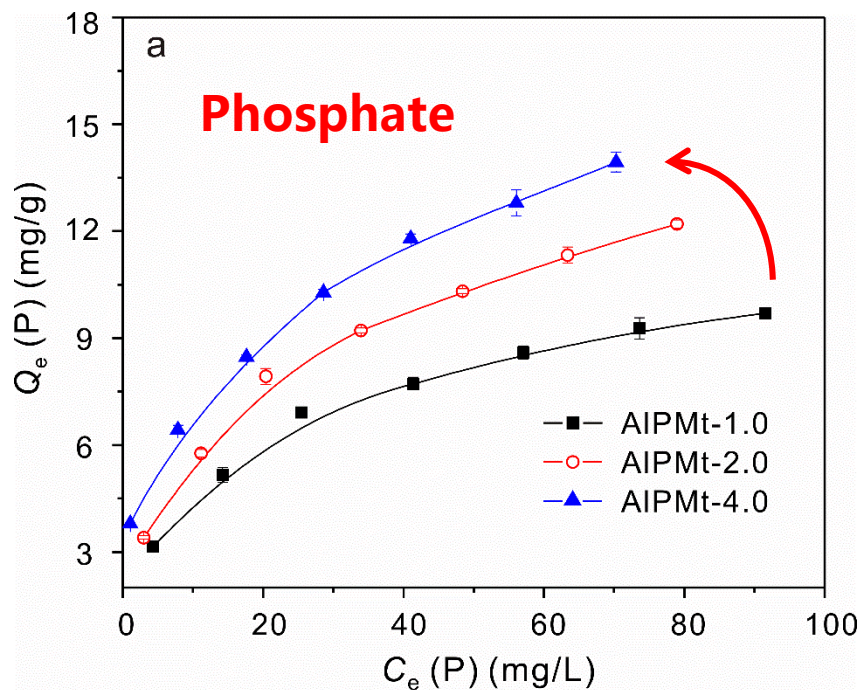


# Zeta potential



Zeta potential of Mt under different solution pH

# Single adsorption system

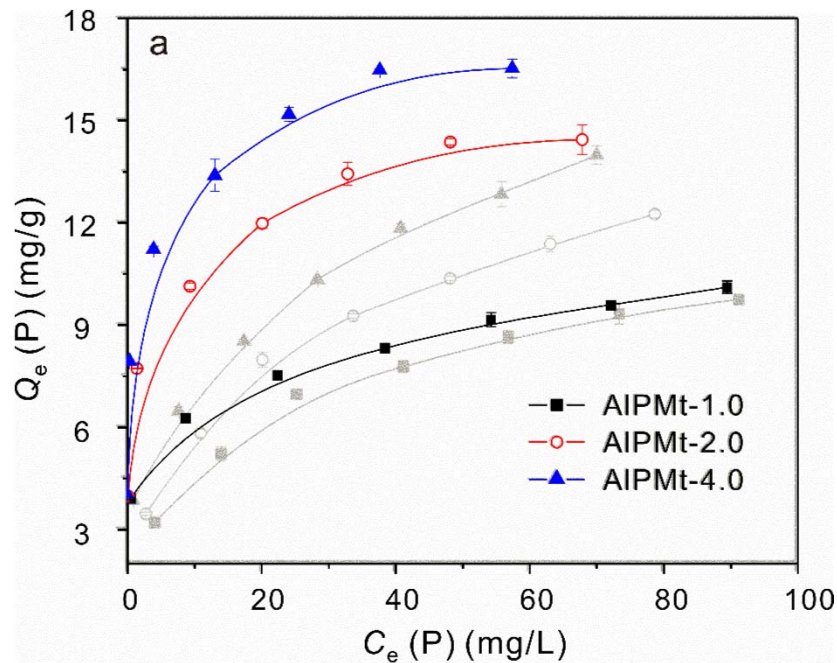


Adsorption isotherms of phosphate and  $\text{Cd}^{2+}$  in single adsorption system

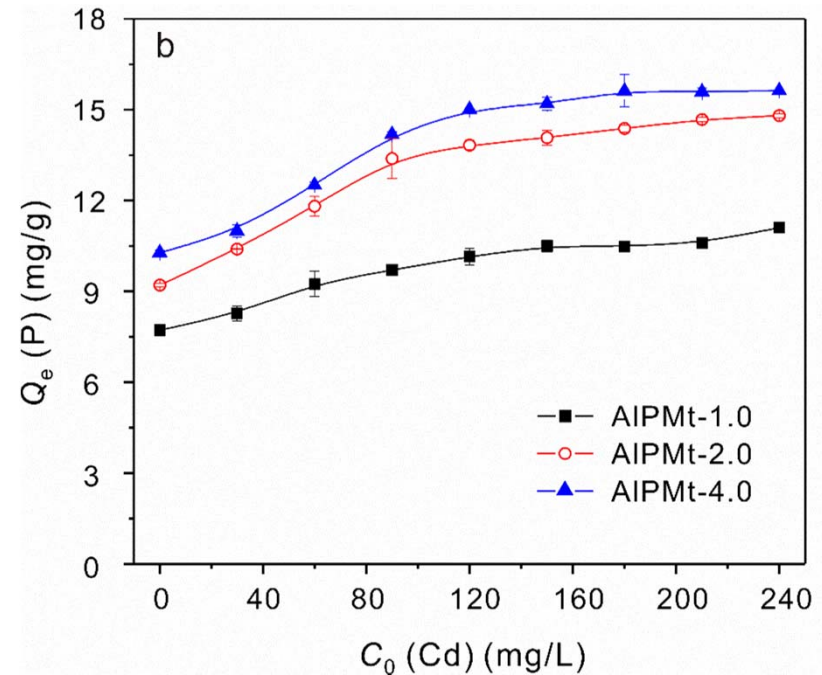
**$\text{Al}_{13}$  enhance the adsorption of phosphate , but not for  $\text{Cd}^{2+}$**

- $\text{pH} < \text{pH}_{\text{zpc}}$  , positive charged surface ;
- $\text{Al}_{13}$  cannot be changed by  $\text{Cd}^{2+}$ .

# Adsorption of phosphate in co-adsorption system



Adsorption isotherm of phosphate  
( $C_{Cd} = 90 \text{ mg/L}$ )



The effect of initial concentration of  $Cd^{2+}$

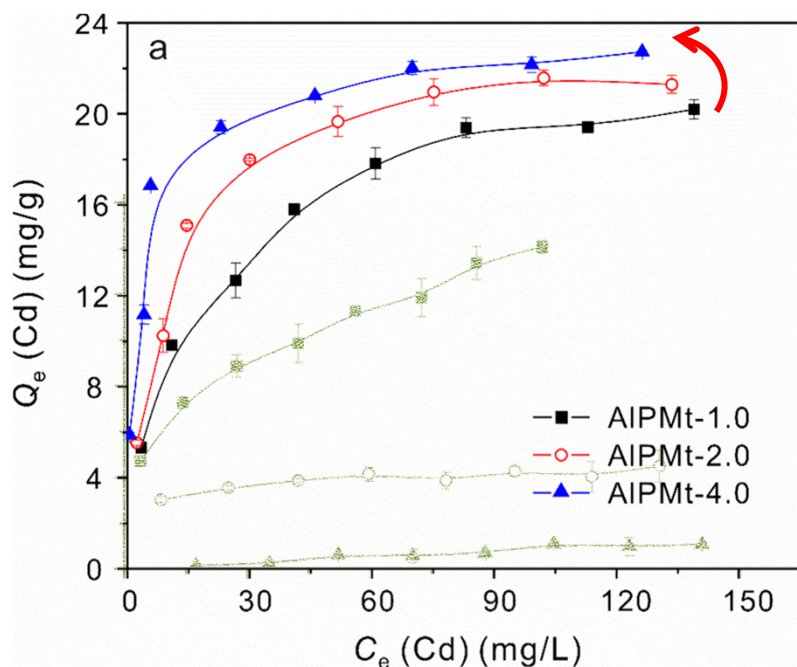
- $Al_{13}$  content
- Initial concentration of  $Cd^{2+}$



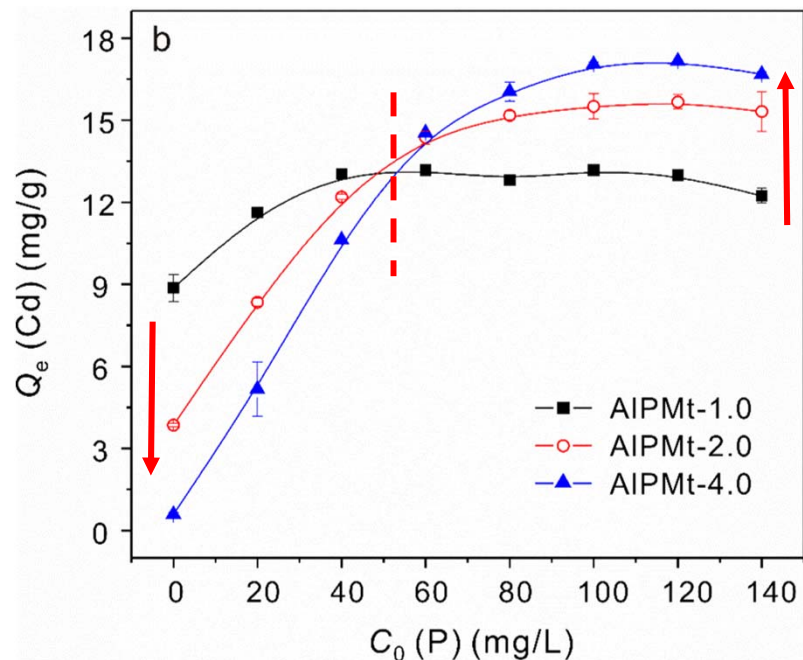
The enhancement of  
phosphate adsorption



# Adsorption of $\text{Cd}^{2+}$ in co-adsorption system



Adsorption isotherms of  $\text{Cd}^{2+}$   
( $C_{\text{phosphate}} = 80 \text{ mg/L}$ )



Effect of initial concentration of phosphate

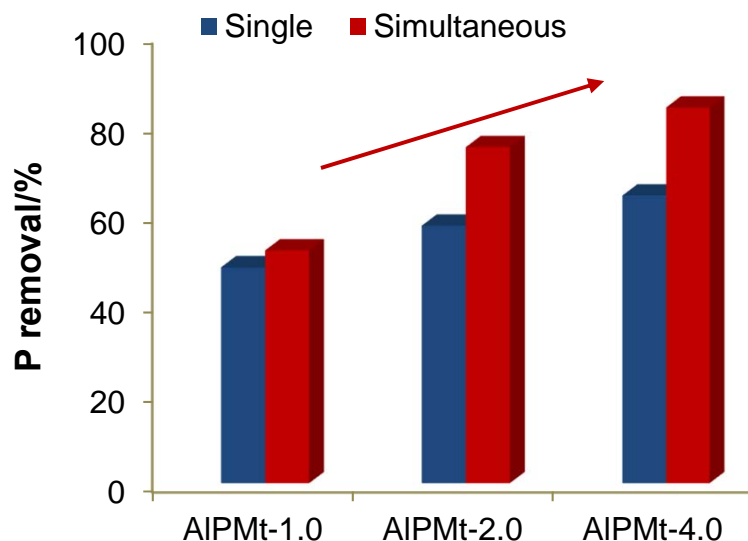
- $\text{Al}_{13}$  content
- initial concentration of phosphate



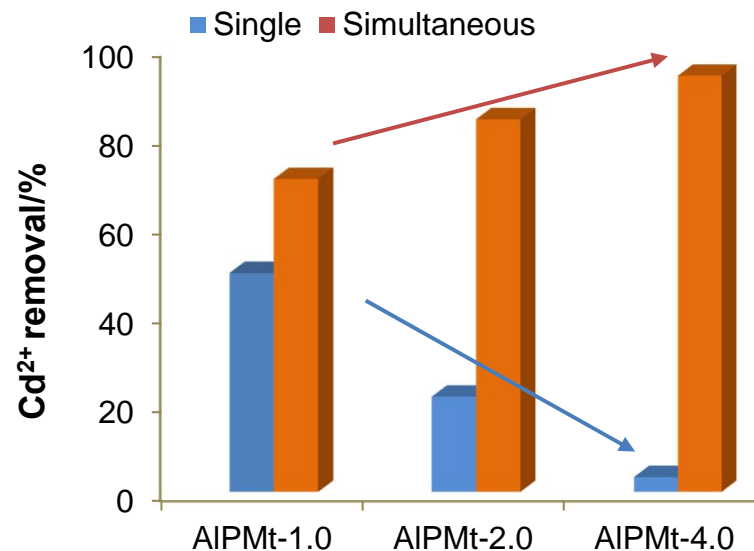
The adsorption of  $\text{Cd}^{2+}$  dramatically increase

# The co-adsorption of phosphate and $\text{Cd}^{2+}$

## Phosphate



## $\text{Cd}^{2+}$

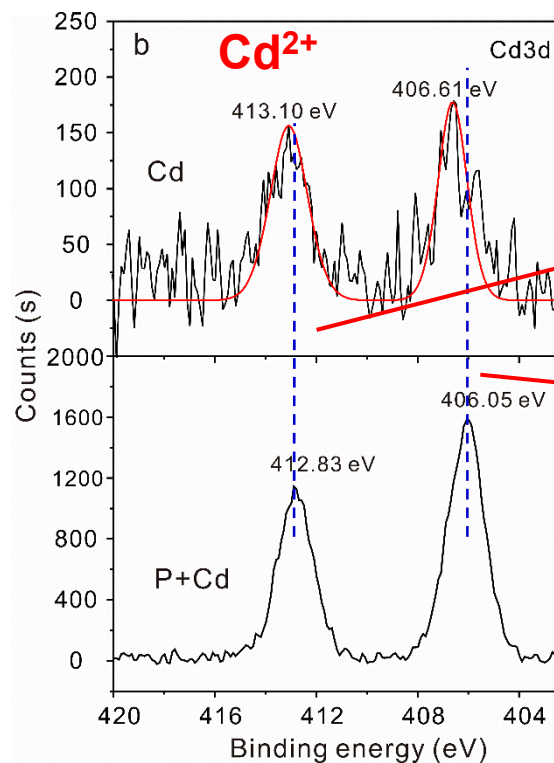
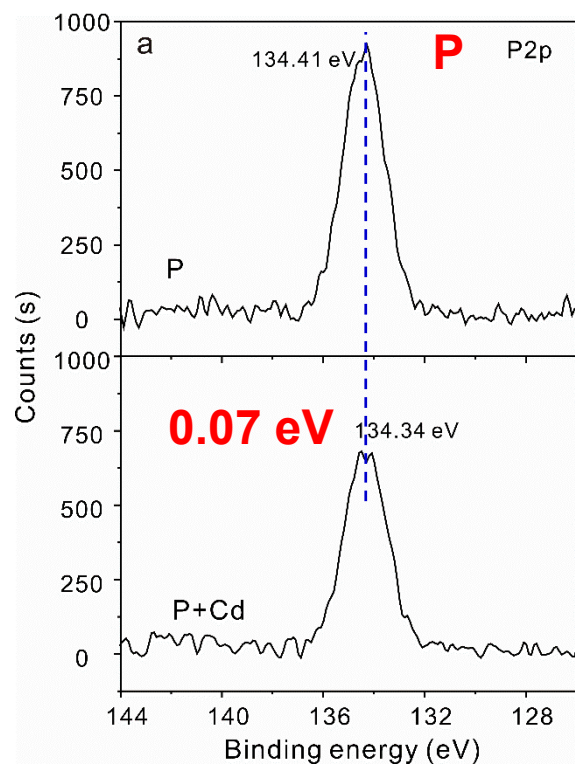


The removal of phosphate and  $\text{Cd}^{2+}$  in single and simultaneous systems

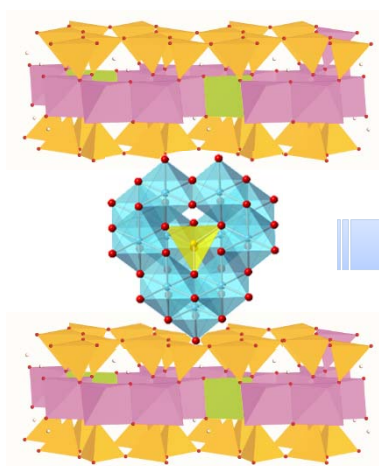
- The enhancement of the adsorption of  $\text{Cd}^{2+}$  was higher than that of phosphate.
- The adsorption sites of  $\text{Cd}^{2+}$  were primarily provided by the adsorbed phosphate on AIPMt.

The co-adsorption sites are mainly existed on the surface of  $\text{Al}_{13}$  cations

# XPS analysis of AlPMt-4.0



The XPS spectrums of P2p and Cd3d on AlMt-4.0 in two adsorption system



**P-bridge ternary surface complexes**

# Conclusion

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- The adsorption of both phosphate and  $\text{Cd}^{2+}$  on ALPMts increased with the increase of loaded amount of  $\text{Al}_{13}$  cation, so did the enhancement of adsorption capacity of ALPMt toward both ions in co-adsorption system.
- The adsorption capacity of ALPMts with higher loaded amount of  $\text{Al}_{13}$  cations toward  $\text{Cd}^{2+}$  were significantly promoted in simultaneous adsorption system, indicating that the surface of intercalated  $\text{Al}_{13}$  cation were the co-adsorption sites.
- The formation of phosphate-bridge ternary surface complexes might be primarily responsible for the co-adsorption of phosphate and  $\text{Cd}^{2+}$  on ALPMt.

## Further work

- The co-adsorption mechanism need to be further studied to clarify the binding model
- solution pH, ion strength, desorption, etc



# SPONSORS



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**Thanks for your attention!**