

Article



Influence of Salinity on the Removal of Ni and Zn by Phosphate-Intercalated Nano Montmorillonite (PINM)

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Abstract: The salinity influence on the adsorptions of Ni and Zn onto phosphate-intercalated nano montmorillonite (PINM) were investigated. Single adsorption isotherm models fitted the single adsorption data well. The adsorption capacity of Ni was higher than that of Zn onto PINM at different salinities. The single adsorption parameters from Langmuir model (Q_{mL} and b_L) were compared with the binary adsorption (Q_{mL}^* and b_L^*). The Q_{mL}^* of Zn was lower than that of Ni. The simultaneous presence of Ni and Zn decreased the adsorption capacities. The single and binary adsorptions onto PINM were affected by the salinity. The competitive Langmuir model (CLM), P-factor, Murali and Aylmore (M–A) models, and ideal adsorbed solution theory (IAST) were satisfactory in predicting the binary adsorption data; the CLM showed the best fitting results. Our results showed that the PINM can be used as an active Ni and Zn adsorbent for a permeable reactive barrier (PRB) in the remediation of saline groundwater.

Keywords: adsorption; binary; nickel; salinity; zinc

1. Introduction

Removal of heavy metal-contaminated groundwater in coastal regions has become an urgent issue due to overuse of the limited amount of freshwater by industrial activities [1]. As industrial activities increase, demand for clean water is also expanding, causing a shortage of freshwater supplies and an increase in wastewater containing heavy metals into the surrounding environment [1,2]. Ni and Zn are commonly found heavy metals in wastewaters from industrial activities including mining, steel processing, electroplating and the production of batteries and paints [2]. Ni and Zn were found at alarming quantities around a metal refinery factory in Korea [3,4]. Furthermore, the Ni was detected up to 171 ppb in the Nakdong River, where refinery wastewater was discharged. Besides Korea, a health risk assessment has been conducted to the Ni- and Zn-contaminated groundwaters from the surrounding industrial areas, steel refineries, and mining sites in the other countries, in order to determine the Ni and Zn concentration limits according to the chronic daily intake (CDI) and the health risk index (HRI) [5–7]. Human body Ni and Zn exposures are strongly related to various health effects, ranging from common symptoms such as dermatitis, nausea, and diarrhea [8], to chronic symptoms such as cancer when the Ni and Zn concentration are above their threshold (>3000 μ g·L⁻¹) [9,10]. In order to meet the need for clean fresh water, several technologies for Ni- and Zn-contaminated groundwater remediation, such as chemical treatment (oxidation), biological processes using bacteria or plants, and physical treatment using permeable reactive barriers (PRBs), have been developed on full-scale [11]. Among these, the physical treatment using PRB is the most cost-effective technique (USD 60-245/ton) compared to the chemical treatment (USD 60-290/ton) and the biological processes

(USD 50,000–200,000/acre), respectively [11]. PRB is a passive remediation technology installed along the way of groundwater flows, where it has the ability to retain heavy metal contaminants [12]. PRBs contain various low-cost reactive adsorbents such as zeolite, hydroxyapatite, or limestone [11,12], creating the system that can stop the mobilization of Ni and Zn in the groundwater.

Montmorillonite has been used to remove Ni and Zn from wastewater through an ion exchange mechanism [2,13]. Its specific surface area and cation exchange capacity (CEC) play more important role in increasing the removal efficiency of Ni at the initial concentration (C₀) of 5.87 mg·L⁻¹ (% removal > 99%) and Zn at the C₀ of 6.54 mg·L⁻¹ (% removal > 99%) [13], than other adsorbents such as zeolite (% removal of Ni = 86.5%, % removal of Zn = 71% [14]), bentonite (% removal of Ni = 29.8% [15], % removal of Zn = 82.4% [16]), and vermiculate (% removal of Ni = 33%, % removal of Zn = 32% [13]). To increase the heavy metal adsorption capacity, several studies have reported techniques for montmorillonite modification, such as modifications using sodium dodecyl sulfate [17] and montmorillonite modified with sodium [18] for Cu and Zn adsorption. Recently, hydroxyiron-modified montmorillonite [19] and ammonium cations-montmorillonite [20] were also developed for As and Cr removal, respectively, with satisfactory results owing to the increase of montmorillonite (PINM) successfully removed the radioactive waste of Cs⁺, Sr²⁺, and Co²⁺ from aqueous solution [21]. However, the application of PINM in the Ni and Zn-contaminated groundwater has not been investigated.

The Ni and Zn removal from groundwater in the vicinity of coastal regions was studied, where the seawater intrusion and salinization continuously affected the groundwater quality [22]. The Ni and Zn binary system can also affect the use of PINM as a reactive adsorbent in the PRB system. Therefore, it is crucial to study the adsorption of Ni and Zn binary system onto the PINM in the saline water.

We focus on the investigation of single and binary adsorption of Ni and Zn onto PINM. For single adsorption, the Langmuir, Feundlich, Dubinin Radushkevich (D–R), Sips, Kargi and Ozmihci (K–O), and Holl-Kirch (H–K) models were used. To the author's knowledge, this is the first attempt to study the influence of salinity on the adsorption of Ni and Zn onto PINM in the binary system. The competitive Langmuir model (CLM), P-factor, Murali and Aylmore (M–A) models, and ideal adsorbed solution theory (IAST) were applied to the binary adsorption data. The feasibility of PINM as a PRB material was evaluated by correlating its physicochemical properties with the parameters of single and binary adsorption.

2. Experimental

2.1. Chemicals

The montmorillonite-KSF (Sigma-Aldrich Chemical Co., St. Louis, MO, USA) was used to prepare PINM. Zinc nitrate (Zn(NO₃)₂, <98%, Kanto Chemical Co., Tokyo, Japan) and nickel nitrate (Ni(NO₃)₂, Aldrich Chemical Co. <98%) were used as adsorbates. NaCl (Sigma-Aldrich, 99.5%), KCl (99.0%, OCI Company Ltd., Seoul, Korea), CaCl₂·2H₂O (Yakuri Pure Chemicals Co., Kyoto, Japan, 70.0–78.0%), MgCl₂ (98%, Duksan Pure Chemicals Co., Ltd., Ansan-si, Korea), NaHCO₃ (99.5%, Sigma-Aldrich), and MgSO₄ (99.0%, Duksan Pure Chemicals Co., Ltd.) were used to prepare artificial seawater. The chemical compositions of artificial seawater (30‰) were demonstrated in Table 1 [23].

Ingredient	Concentration (g/L)
NaCl	24.72
KCl	0.67
CaCl ₂ ·2H ₂ O	1.36
MgCl ₂	2.18
MgSO ₄	3.07
NaHCO ₃	0.18

Table 1. The chemical compositions of artificial seawater (30‰).

2.2. The Adsorbent Preparation and Characterization

The montmorillonite–KSF was purified using hydrogen peroxide (H₂O₂; 30%, Duksan Chemical Co.) followed by washing using distilled and deionized (DDI) water (MilliporeSigmaTM SynergyTM Ultrapure Water Purification System, Thermo Fisher Scientific, Waltham, MA, USA) at 60 °C, and drying at 60 °C for 24 h. PINM was synthesized from the purified montmorillonite mixed with 2000 mg/L of PO₄^{3–} (KH₂PO₄; >98%, Yakuri Pure Chemicals Co.) using a rotary agitator in room temperature at 200 rpm for 24 h, followed by three times washing using 1 L of DDI water to remove excess H₂PO₄[–] ions, and air-dried for 3 days [21].

The physicochemical properties of the adsorbents were characterized. Determination of pH of point of zero charge (pH_{PZC}) of PINM was conducted by following the method by Ma et al. [21]. Cation exchange capacity (CEC) of PINM and montmorillonite were measured by the standard method [24]. Brunauer–Emmett–Teller (BET) surface area (A_{BET}) was determined from N₂ adsorption/desorption isotherm data (ASAP-2010 specific surface area analyzer, Micromeritics, Norcross, GA, USA) and fitted to the BET model. Pore size distribution was calculated using the Barrett Joyner Halenda (BJH) adsorption model (Quantachrome, Autosorb-iQ & Quadrasorb Si, Boynton Beach, FL, USA) and a specific surface area analyzer (Quantachrome, Nova, 2000, Boynton Beach, FL, USA). Scanning electron microscopy (SEM, Hitachi S–4200, Chiyoda City, Tokyo, Japan) was used to determine the morphology of montmorillonite before and after modification. The chemical composition of PINM and montmorillonite were characterized by EDS analysis (E–MAX EDS detector, Horiba, Kyoto, Japan). X–ray diffraction (XRD) patterns were measured using an X-ray diffractometer (PW2273 diffractometer, Philips, Guildford, UK) using Cu K α radiation ($\lambda = 1.54$ Å) in the range from 5° to 50° of 2 θ at a step size of 0.02° and a step time of 1 s.

2.3. Adsorption Isotherm Experiments

For single adsorption, the experiments were performed in 50 mL conical centrifuge tube (polyethylene, SPL Labware, Pocheon-si, Gyeonggi-do, Korea) at 25 °C. Firstly, 1.0 g of PINM was prepared in 50 mL tubes. The solution of Ni^{2+} and Zn^{2+} dissolved in artificial seawater (30‰) and DDI water (0‰), respectively, were added into the tubes. Eight heavy metal solutions (Ni: 0.017, 0.085, 0.170, 0.340, 0.681, 1.022, 1.363 and 1.704 mM; Zn: 0.015, 0.076, 0.153, 0.306, 0.612, 0.918, 1.224 and 1.530 mM) were used. For controlling the solution pH at 5.0, 0.05 M MES buffer (2-[N-morpholino]ethanesulfonic acid hydrate; 99.5%, ACROS Organics, Morris Plains, NJ, USA) was used. The NaNO₃ (≥99%, Sigma–Aldrich) at the concentration of 0.01 M was used as a background electrolyte. The use of MES buffer did not form complexation reactions with heavy metals as confirmed by the results of others [25]. To prevent the formation of metal hydroxides and carbonates, the solution pH was controlled. The program of MINEQL⁺ version 4.6 for Windows (Environmental Research Software, Hallowell, ME, USA) was used to predict the molar distributions of nickel and zinc species at pH 5.0. To eliminate the carbon dioxide effect on adsorption, the headspace in the vials were minimized. The sample was mixed using a tumbler at 10 rpm for 24 h. Preliminary kinetic experiments showed that adsorption equilibrium was reached within 3 h. However, adsorption experiments were conducted for 24 h throughout this study to ensure adsorption equilibrium. The vials were collected and followed by the centrifugation at 3000 rpm (=1977 g) for 20 min. Then, the supernatant was filtered using 0.2 μ m

syringe filter (Whatman, cellulose nitrate membrane filter, $\phi = 25$ mm). The preliminary study showed that the cellulose nitrate membrane filter had no effect on sorption of the Ni and Zn. The Ni and Zn concentration in the aqueous phase was analyzed using an inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2100 DV, Perkin-Elmer Co., Industry Drive Pittsburgh, PA, USA). Duplicate experiments were performed.

Metal solution at the same molar concentration (0.0170, 0.085, 0.170, 0.340, 0.681, 1.022, 1.363 and 1.704 mM) in a 1:1 volume ratio for each solute were prepared for binary adsorption experiments (Ni/Zn). The adsorption experiment in the binary system were performed in the same manner as those in the single system.

2.4. Isotherm Equations and Fitting Method

Single and binary adsorption models are summarized in Table 2.

	F (*	D (
Model	Equation	Keterence
Single Adsorption		
Freundlich $C_s = K_F C_w^{N_F}$	(1)	
Langmuir $C_s = rac{Q_{mL}b_LC_w}{1+b_LC_w}$	(2)	
Dubinin-Radushkevich (D-R) $C_s = Q_{mD} \exp(-\beta \varepsilon^2)$	(3)	[26,27]
$E = \frac{1}{\sqrt{2\beta}}$	(4)	
$C_s = rac{ ext{Sips}}{ extsf{2ms}(b_S C_w)^{N_S}} onumber \ 1+(b_S C_w)^{N_S}$	(5)	[28]
Kargi–Ozmihci (K–O) $C_s = \frac{Q_{mG}C^{N_G}}{K+C^{N_G}}$	(6)	[29]
Holl-Kirch (H–K) $C_{s} = \frac{Q_{mHK}b_{HK}C_{w}{}^{N_{HK}}}{1+b_{HK}C_{w}{}^{N_{HK}}}$	(7)	[30,31]
Binary Adsorption		
Competitive Langmuir model (CLM) $C_{s,i} = \frac{Q_{mL_i}b_{L,i}C_{w,i}}{1 + \sum_{j=1}^{N} b_{L,j}C_{w,j}}$	(8)	[32]
$P-factor P_i = \frac{Q_{mL,i}}{Q_{mL,i}}$	(9)	[22]
$C_{s,i} = rac{1}{P_i} rac{b_{L,i}Q_{mL,i}C_{w,i}}{1+b_{L,i}C_{w,i}}$	(10)	[55]
Murali–Aylmore (M–A)		
$C_{s,i} = rac{K_{Fi}C_{w,i}^{N_i+1}}{\sum\limits_{j=1}^{N}a_{ij}C_{w,j}}$	(11)	[34]
Ideal adsorbed solution theory (IAST) $\pi = \frac{RT}{A} \int_0^{q_1^*} \frac{\ln C_1}{\ln q_1} dq_1 = \frac{RT}{A} \int_0^{q_1^*} \frac{\ln C_2}{\ln q_2} dq_2 = \dots = \frac{RT}{A} \int_0^{q_N^*} \frac{\ln C_N}{\ln q_N} dq_N$ or $\pi = \frac{RT}{A} \int_0^{C_1^*} \frac{q_1}{C_1} dC_1 = \frac{RT}{A} \int_0^{C_2^*} \frac{q_2}{C_2} dC_2 = \dots = \frac{RT}{A} \int_0^{C_N^*} \frac{q_N}{C_N} dC_N$	(12)	[35–37]

3. Results and Discussion

3.1. Adsorbent Characteristics

The raw montmorillonite and PINM physicochemical properties were compared. The A_{BET} and pore volume remarkably increased from 2.6 m²/g to 115.9 m²/g and from 0.011 cm³/g to 0.1 cm³/g, respectively, due to the strongly adsorbed phosphate ions through the formation of Al-O-P-OH surface precipitates and an inner–sphere complex [32]. The pore size also slightly increased from 38.05 Å to 40.73 Å. As shown in Figure 1, SEM images showed that the raw montmorillonite particle size was bigger than that of PINM. However, the CEC of PINM (58.1 meq/100 g) was higher than that of raw montmorillonite (52.7 meq/100 g). Due to the H⁺ displacement, the pH_{PZC} values of raw montmorillonite decreased from pH 5.5 to 4 after phosphate-intercalation. The results of chemical analysis were obtained by EDS data, presented in Figure 1. In the intercalation process, Ca in the montmorillonite (Figure 1c) disappeared and was replaced by P in the PINM (Figure 1d). The O in the montmorillonite was slightly reduced in the PINM. However, the Si spectra did not change. This result indicated a successful modification of montmorillonite to become PINM, which was in good agreement with the literature [21].



Figure 1. SEM images of (**a**) montmorillonite and (**b**) PINM, and EDS spectra of (**c**) montmorillonite and (**d**) PINM.

The X–ray diffraction (XRD) patterns of the PINM and montmorillonite are illustrated in Figure 2. As the phosphate-intercalation expanded the interlayer spaces [21], the basal spacing of PINM (15.33 Å) was larger than that of raw montmorillonite (12.07 Å). These results successfully confirm the phosphate-intercalated nano montmorillonite. Crystal size of montmorillonite and PINM were calculated at optimum peak intensity of montmorillonite (19.8°) and PINM (19.8°) using the Scherrer equation, where the crystal size of montmorillonite (322.7 nm) was bigger than that of PINM (34.2 nm). This result suggests that the modification using phosphate decreased the montmorillonite crystal size.



Figure 2. XRD analyses of montmorillonite and PINM.

3.2. Ni and Zn Adsorption

The effects of saline water on the adsorption capacities of single adsorption, Ni and Zn onto PINM at pH 5.0 were expressed in Figure 3. The single adsorption data were fitted by 2-parameter isotherm models (the Freundlich, Langmuir, and D–R models) and the model parameters for PINM are listed in Table 3. All models were fitted well to the experimental data (Freundlich: $0.95 < R^2 < 0.99$, Langmuir: $0.98 < R^2 < 0.99$, and DR: $0.97 < R^2 < 0.98$).



Figure 3. Single adsorption of Ni and Zn onto PINM at different salinities (pH = 5.0). (**a**) 0‰ and (**b**) 30‰. Lines represent adsorption models.

The Freundlich isotherm has been extensively used to define adsorption of heavy metal ions onto clay [38] and considers the adsorption affinity and nonlinearity. This shows that the adsorption of Ni and Zn mainly occurred onto the PINM surface active sites. The K_F value for 0‰ was higher than K_F value for 30‰ at pH 5.0 due to less solubility in saline water. The K_F values of Zn were consistently higher than those of Ni. The Freundlich exponent, N_F , is the heterogeneity factor indicate as $0.1 < N_F < 1$; favorable adsorption process [39,40]. The N_F values for adsorptions of Ni and Zn onto adsorbents were in the range of 0.39–0.46, indicating that both Ni and Zn adsorption was favorable [41].

Freundlich	Metal	Salinity (‰)	<i>K_F</i> [(mmol/g)/(mmol/L) ^{<i>N_F</i>]}	N _F (-)	R^2	SSE	
	Ni	0	0.337 ± 0.005	0.425 ± 0.016	0.994	0.001	
		30	0.239 ± 0.008	0.464 ± 0.038 0.957		0.006	
	Zn	0	0.282 ± 0.006	0.423 ± 0.021	0.987	0.002	
		30	0.115 ± 0.003	0.392 ± 0.033	0.950	0.002	
Langmuir	Metal	Salinity (‰)	Q_{mL} (mmol/g)	b _L (L/mmol)	R ²	SSE	S_{f}
	Ni	0	0.383 ± 0.017	4.937 ± 0.767	0.986	0.003	0.910
		30	0.319 ± 0.015	2.988 ± 0.378	0.982	0.002	0.944
	Zn	0	0.314 ± 0.014	5.171 ± 0.751	0.983	0.003	0.906
		30	0.147 ± 0.005	4.055 ± 0.490	0.977	0.001	0.925
D-R	Metal	Salinity (‰)	Q_{mD} (mmol/g)	$\beta ({ m mol}^2/{ m J}^2, imes 10^{-8}),$	R ²	SSE	E (kJ/mol)
	Ni	0	0.330 ± 0.011	2.394 ± 0.264	0.975	0.006	4.57
		30	0.263 ± 0.008	3.799 ± 0.319	0.972	0.004	3.63
	Zn	0	0.274 ± 0.009	2.443 ± 0.242	0.973	0.004	4.52
		30	0.128 ± 0.004	3.170 ± 0.251	0.970	0.001	3.97
Sips	Metal	Salinity (‰)	Q_{mS} (mmol/g)	b _S (L/mmol)	N_S	R^2	SSE
	Ni	0	0.670 ± 0.087	0.945 ± 0.387	0.604 ± 0.036	0.998	0.000
		30	0.323 ± 0.041	2.897 ± 0.911	0.982 ± 0.147	0.979	0.002
	Zn	0	0.492 ± 0.096	1.407 ± 0.854	0.640 ± 0.069	0.993	0.001
		30	0.153 ± 0.017	3.627 ± 1.094	0.928 ± 0.150	0.972	0.001
К-О	Metal	Salinity (‰)	Q_{mKO} (mmol/g)	b_{KO} (L/mmol)	N_{KO}	R^2	SSE
	Ni	0	0.670 ± 0.087	1.034 ± 0.254	0.604 ± 0.036	0.998	0.000
		30	0.323 ± 0.041	0.352 ± 0.160	0.982 ± 0.147	0.978	0.002
	Zn	0	0.492 ± 0.096	0.804 ± 0.330	0.640 ± 0.069	0.993	0.001
		30	0.153 ± 0.017	0.303 ± 0.139	0.928 ± 0.150	0.972	0.001
H–K	Metal	Salinity (‰)	Q_{mHK} (mmol/g)	b _{HK} (L/mmol)	N _{HK}	R^2	SSE
	Ni	0	0.670 ± 0.087	0.967 ± 0.237	0.604 ± 0.036	0.998	0.000
		30	0.323 ± 0.041	2.844 ± 1.292	0.982 ± 0.147	0.978	0.002
	Zn	0	0.492 ± 0.096	1.244 ± 0.511	0.640 ± 0.069	0.993	0.010
		30	0.153 ± 0.017	3.305 ± 1.518	0.928 ± 0.150	0.972	0.001

Table 3. Adsorption model parameters for single adsorption of Ni and Zn onto PINM at pH 5. * Calculated at $C_{w,0} = 0.02$ mM.

Note: SSE = sum of squared estimate of error.

In the previous studies, the adsorption capacities of montmorillonite and various modified montmorillonite were compared in Table 4. The maximum adsorption capacity (Q_{mL}) of Ni and Zn at 0‰ in this study was higher than that of Ni and Zn at 30‰. The Q_{mL} values of Ni were higher than those of Zn. The Langmuir parameter, named separation factor (S_f) describes that adsorption isotherm can be favorable ($0 < S_f < 1$), unfavorable ($S_f > 1$), linear ($S_f = 1$), or irreversible ($S_f = 0$) [42,43]:

$$S_f = \frac{1}{1 + b_L C_{w,0}}$$
(13)

The calculated values of S_f ranged 0.90 and 0.94 (Table 3), indicating that adsorptions of Ni and Zn onto PINM are favorable.

The D–R model parameter also fitted well to the single adsorption data ($0.97 < R^2 < 0.98$). The Q_{mD} value of the D–R model increased in the order of 0% > 30‰ for both Ni and Zn at pH 5.0. The Q_{mD} values of D–R model were slightly less than the Q_{mL} values of the Langmuir model (Table 3). The value of *E* in D–R model can be used to differentiate the adsorption mechanisms (physical or chemical). When the *E* value is in the range of 8 to 16 kJ/mol, the adsorption occurs by ion-exchange. The *E* value less than 8 kJ/mol indicates the physical adsorption process, whereas *E* value greater than 16 kJ/mol, the adsorption is chemical [44]. The calculated *E* values in this study were less than 4.6 kJ/mol indicating that adsorption of Ni and Zn onto PINM occurs via physical adsorption in nature [27].

By using the nonlinear regression method, three-parameters adsorption models such as Sips, K–O and H–K models were fitted to the adsorption data (Table 3). In terms of R^2 values, the Sips (0.97 < R^2 < 0.99), K–O (0.97 < R^2 < 0.99) and H–K (0.97 < R^2 < 0.99) models were slightly better than the Freundlich (0.95 < R^2 < 0.99), Langmuir (0.98 < R^2 < 0.99), and D–R (0.97 < R^2 < 0.98) models.

The comparison of adsorption capacity by Freundlich adsorption coefficient (K_F), Langmuir adsorption capacity (Q_{mL}) and D–R adsorption capacity (Q_{mD}) in Table 3, Ni was higher than Zn for both 0‰ and 30‰ containing PINM at pH 5.0. The maximum adsorption capacity (Q_{mS} of the Sips model, Q_{mK} of K–O model and Q_{mK} of H–K model) at 0‰ was higher than those of 30‰ for both metals. The maximum capacity of values of Ni were higher than Zn at the same salinity. Several literatures have reported similar results (adsorption capacities of Ni > that of Zn) for adsorbents such as Na-montmorillonite [18]. The adsorption affinity of Ni and Zn decreased with the increase salinity (30‰) owing to competition between the added metals and cations in background solution by the limited cation exchange sites [45–47]. Table 3 summarizes the comparison of Ni and Zn sorption capacities of Langmuir model for various adsorbents found in literature. The Q_{mL} values of Ni onto PINM in this study were slightly higher than those of Ni onto montmorillonite in the literature [48,49].

Heavy Metals	Adsorbents	Adsorption Capacity (Q _{mL} , mmol/g)	Reference
Ni	PINM	0.383	This study
	Montmorillonite	0.360	[48]
	Na-Montmorillonite	0.002	[50]
Zn	PINM	0.314	This study
	Na-montmorillonite	0.001	[50]

Table 4. Adsorption capacity of Ni and Zn by various adsorbents.

3.3. Ni/Zn Adsorption

Binary adsorption of Ni and Zn onto PINM at different salinities were presented in Figure 4. The binary adsorption data of Ni and Zn onto PINM and the predictions of M–A, CLM, P-factor and IAST models are shown in Figure 4 (Table 5).



Figure 4. Binary adsorption of Ni and Zn onto PINM at different salinities (pH = 5.0). (**a**) 0‰ and (**b**) 30‰. Lines represent model predictions.

Table 5. M-A model, CLM, P-factor model and IAST coupled to single adsorption model parameters for binary adsorption of Ni(1) and Zn(2) onto PINM at pH 5.

Salinity (‰)	<i>a</i> ₁₂	<i>a</i> ₂₁	<i>R</i> ²	SSE	RMSE
0	0.053 ± 0.042	0.297 ± 0.069	0.866/0.749	0.028/0.021	0.041/0.035
30	0.576 ± 0.028	0.333 ± 0.090	0.984/0.820	0.001/0.004	0.008/0.017
Salinity (‰)	-	-	<i>R</i> ²	SSE	RMSE
0			0.869/0.861	0.128/0.067	0.090/0.065
30			0.934/0.908	0.013/0.006	0.030/0.021
Salinity (‰)	Pi	-	<i>R</i> ²	SSE	RMSE
0	1.175/1.570		0.948/0.894	0.050/0.051	0.058/0.058
30	1.253/0.747		0.929/0.299	0.014/0.048	0.033/0.061
Salinity (‰)	-	-	R ²	SSE	RMSE
0			0.918/0.924	0.080/0.037	0.073/0.049
30			0.881/0.809	0.091/0.013	0.084/0.032
Salinity (‰)	-	-	<i>R</i> ²	SSE	RMSE
0			0.882/0.867	0.115/0.064	0.088/0.065
30			0.964/0.699	0.007/0.021	0.023/0.040
Salinity (‰)	-	-	R ²	SSE	RMSE
0			0.905/0.823	0.093/0.085	0.079/0.075
30			0.965/0.832	0.007/0.012	0.023/0.030
Salinity (‰)	-	-	<i>R</i> ²	SSE	RMSE
0			0.882/0.867	0.115/0.064	0.088/0.065
30			0.964/0.700	0.007/0.021	0.023/0.040
	Salinity (%•) 0 30 Salinity (%•) 0 30	Salinity (%•) a12 0 0.053 ± 0.042 30 0.576 ± 0.028 Salinity (%•) - 0 - 30 - 0 1.175/1.570 30 1.253/0.747 Salinity (%•) - 0 1.253/0.747 Salinity (%•) - 0 30 Salinity (%•) - 0 30 Salinity (%•) - 0 30 Salinity (%•) - 0 - 0 30 Salinity (%•) - 0 30 30 - 0 - 30 - 0 - 30 -	Salinity (%) a_{12} a_{21} 0 0.053 ± 0.042 0.297 ± 0.069 30 0.576 ± 0.028 0.333 ± 0.090 Salinity (%)0 $ -$ 0 $ -$ 30 P_i $-$ Salinity (%) P_i $-$ 0 $1.175/1.570$ $-$ 30 $1.253/0.747$ $-$ Salinity (%) $ -$ 0 30 $-$ 0 30 $-$ 0 30 $-$ 0 30 $-$ 0 30 $ 0$ 30 $-$	Salinity (%o) a_{12} a_{21} R^2 00.053 ± 0.0420.297 ± 0.0690.866/0.749300.576 ± 0.0280.333 ± 0.0900.984/0.820Salinity (%o) R^2 00-0.869/0.8613000.934/0.908Salinity (%o) P_1 - R^2 01.175/1.5700.948/0.894301.253/0.7470.948/0.894301.253/0.7470.948/0.894301.253/0.7470.948/0.89430 R^2 0 R^2 0 R^2 0 R^2 0 R^2 0-0.948/0.89430-0.918/0.9240 R^2 0 R^2	Salinity (%o) a_{12} a_{21} R^2 SSE0 0.053 ± 0.042 0.297 ± 0.069 $0.866/0.749$ $0.028/0.021$ 30 0.576 ± 0.028 0.33 ± 0.090 $0.984/0.820$ $0.001/0.004$ Salinity (%o) R^2 SSE0 $1.175/1.570$ $0.948/0.894$ $0.050/0.051$ 30 $1.175/1.570$ $0.948/0.894$ $0.050/0.051$ 30 $1.253/0.747$ $0.948/0.894$ $0.050/0.051$ 30 $1.253/0.747$ $0.948/0.894$ $0.001/0.048$ Salinity (%o) R^2 SSE0 $1.253/0.747$ $0.918/0.924$ $0.080/0.037$ 30 R^2 SSE0 $1.175/1.570$ $0.918/0.924$ $0.001/0.048$ 30 R^2 SSE0 R^2 SSE0<

Note: SSE = sum of squared estimate of error, RMSE = root mean square error.

In Table 5, the M–A model predicted the binary adsorption well ($0.75 < R^2 < 0.98$). In the M–A model fitting results, the competition factor (a_{ij}) of Zn ($a_{21} = 0.30$) was consistently higher than that of Ni ($a_{12} = 0.05$) at 0‰, which explains that Zn was more affected than Ni in binary competitive adsorption. In contrast to the results at 0‰, the a_{12} (0.58) was higher than the a_{21} (0.33) at 30‰. The values of a_{12} and a_{21} increased from 0.05 to 0.58 and from 0.30 to 0.33 as the salinity increased from 0 to 30‰. This indicates that the competition effect between the two metals are more affected by the presence of co-solutes (Na⁺, K⁺, Ca²⁺, and Mg²⁺) in the seawater [51]. The CLM prediction was well

fitted with the binary adsorption in terms of \mathbb{R}^2 values (0.86 < \mathbb{R}^2 < 0.93). The same is true for the P-factor model prediction (\mathbb{R}^2 > 0.89), except Zn at 30‰. The prediction using IAST varied with single adsorption model and metal solution. For the most binary adsorptions, the IAST predictions were in good agreement with data (Table 5).

Compared to the single adsorptions (Table 3), the Q_{mL} values of binary adsorptions were reduced due to competition (Table 6). In both single and binary adsorptions, the Langmuir parameters, Q_{mL} and b_L , were not correlated. In Table 7, the estimated maximum adsorption capacity values of binary adsorption (Q_{mL}^*) were compared with those of single adsorption (Q_{mL}). The $Q_{mL,Ni}/Q_{mL,Zn}$ and $Q_{mL,Ni}^*/Q_{mL,Zn}^*$ ratios were higher than unity at both 0‰ and 30‰. This suggests the higher adsorption affinity of Ni than Zn, regardless of salinity. The $Q_{mL,i}/Q_{mL,i}^*$ ratios were mostly less than unity, indicating the simultaneous presence of both Ni and Zn reduced adsorption due to competition for adsorption sites in the adsorbent. In addition, $Q_{mL,Ni}/Q_{mL,Ni}^* > Q_{mL,Zn}/Q_{mL,Zn}^*$ at 0‰ but vice versa at 30‰ indicates that Ni adsorption was more affected than Zn adsorption at 0‰ but vice versa at 30‰ in binary adsorption process in the simultaneous presence of a co-solute.

Table 6. Langmuir model parameters for binary adsorption of Ni and Zn onto the sorbents at pH 5.

Salinity (‰)	Solute	Q_{mL}^{*} (mmol/g)	b_L^* (L/mmol)	R^2	SSE
0	Ni in Ni/Zn	0.326 ± 0.015	14.38 ± 3.946	0.918	0.017
	Zn in Ni/Zn	0.200 ± 0.011	64.31 ± 28.61	0.794	0.017
30	Ni in Ni/Zn	0.254 ± 0.016	1.616 ± 0.232	0.986	0.001
	Zn in Ni/Zn	0.196 ± 0.026	0.922 ± 0.227	0.973	0.001

 Q_{mL}^* and b_{mL}^* indicates Q_{mL} value and b_{mL} value for binary competitive adsorption, respectively.

Salinity (‰)	$Q_{mL,Ni}/Q_{mL,Zn}$	$Q_{mL,Ni}^*/Q_{mL,Zn}^*$	$Q_{mL,Ni}/Q_{mL,Ni}^{*}$	$Q_{mL,Zn}/Q_{mL,Zn}^{*}$
0	1.219	1.630	0.851	0.637
30	2.175	1.297	0.798	1.338
Salinity (%)	$b_{L,Ni}/b_{L,Zn}$	$b_{L,Ni}^*/b_{L,Zn}^*$	$b_{L,Ni}/b_{L,Ni}^{*}$	$b_{L,Zn}/b_{L,Zn}^*$
0	0.955	0.224	2.913	12.44
30	0.737	1.752	0.541	0.228

Table 7. Comparison of Q_{mL} and b_L values of single and binary adsorption of Ni and Zn at pH 5.

The affinity constant (b_L) of Langmuir model was calculated from adsorption isotherm data to estimate the free energy change of adsorption [38,52]. Higher b_L values are related to specifically adsorbed metals at high energy surfaces with low dissociation constants. Meanwhile, lower b_L values were related to adsorption at low energy surfaces with high dissociation constants [53]. The binding energy coefficient ($b_{L,Ni}$ and $b_{L,Zn}$ for single adsorption and $b^*_{L,Ni}$ and $b^*_{L,Zn}$ for binary adsorption, respectively) varied with salinity and metal solution. In the single adsorption, the adsorption affinity of Zn was higher than Ni ($b_{L,Zn} > b_{L,Ni}$) at both 0‰ and 30‰. On the other hand, $b^*_{L,Zn} > b^*_{L,Ni}$ at 0‰ and $b^*_{L,Zn} < b^*_{L,Ni}$ at 30‰ were observed for binary competitive adsorption. It was also found that $b_i > b^*_i$ at 0‰, whereas $b_i < b^*_i$ at 30‰. This indicates that co-solute present in the seawater may affect the adsorption affinity of the metals onto PINM.

4. Conclusions

Effect of salinity on the adsorptions of Ni and Zn onto PINM have been investigated using single and bimary systems at pH 5. In single adsorption, Freundlich, Langmuir, D–R, Sips, K–O and H–K models were fitted well. The adsorption affinity (K_F) and capacities (Q_{mL} , Q_{mD} , Q_{mS} , Q_{mKO} , and Q_{mHK}) of Ni were consistently higher than Zn at different salinities. The adsorption capacities of Ni and Zn at 0‰ were slightly higher than at 30‰, mainly owing to the competition between the metals and

cations in solution and solubility. Binary competitive adsorptions were analyzed by the Langmuir model, M–A model, CLM, P-Factor model and IAST predictions. Adsorption capacities of Ni for Langmuir, D–R, Sips, K–O and H–K models are higher than Zn. The competition between Ni and Zn decreased the adsorption retention on the specific sites in the adsorbents. The adsorption capacities of Ni and Zn in the Ni/Zn binary system were lower than those in the single system due to competition. The PINM could be used as a sustainable reactive medium in the PRB application for removing Ni and Zn in the presence of salinity.

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Nomenclature

- *A* interfacial area between the solution and solid adsorbent
- a_{ij} competition coefficient between the solutes; subscripts *i* and *j* denote the solutes
- b_{HK} constant in the H–K model [(L/mmol)^{N_{HK}}]
- b_L site energy factor (L/mmol)
- $b_{L,i}$ Langmuir model parameter obtained from single adsorption (L/mmol)
- *b*_S Sips isotherm constant (L/mmol)
- β constant related to the mean free energy of adsorption per mole of the adsorbate (mol²/J²)
- *C_i* aqueous solution concentration of solute *i* at multi-solute competitive adsorption equilibrium (mmol/L)
- *C*_s solid-phase equilibrium concentration (mmol/g)
- $C_{s,i}$ adsorbed amount of solute *i* at multi-solute competitive adsorption equilibrium (mmol/g)
- *C*_w aqueous-phase equilibrium concentration (mmol/g)
- *E* mean free energy $[(2\beta)^{-0.5}]$ (kJ/mol)
- ε adsorption potential [=*RT* ln(1 + 1/*C*_w)] (J/mol)
- *K* saturation constant (mmol/L)
- K_F Freundlich adsorption coefficient (sorption affinity) [(mmol/kg)/(mmol/L)^{N_F}]
- N total number of solutes
- N_F linearity coefficient (-)
- N_G cooperative binding constant (–)
- N_{HK} constant in the H–K model (–)
- N_S (-) is Sips isotherm exponential constant
- *R* ideal gas constant (J/mol·K)
- *T* absolute temperature (K)
- Q_{mD} theoretical saturation capacity (mg/kg)
- Q_{mG} maximum adsorption capacity of the adsorbent (mmol/g)
- Q_{mHK} constant in the H–K model [($L^{N_{KC}}$ mmol^{1–N_{KC}}/g)]
- Q_{mL} maximum adsorption capacity (mmol/kg)
- $Q_{mL,I}$ maximum adsorption capacity for component *i* in a single system (mmol/g)
- $Q_{mL,i}^*$ maximum adsorption capacity for component *i* in a single system (mmol/g)
- Q_{mS} maximum adsorption capacity (mmol/g)
- π spreading pressure.

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