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Removal of cobalt, strontium and cesium from radioactive laundry wastewater by ammonium molybdophosphate–polyacrylonitrile (AMP–PAN)

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ABSTRACT

Applicability of ammonium molybdophosphate–polyacrylonitrile (AMP–PAN) on the adsorptive removal of Co, Sr and Cs in the radioactive laundry wastewater generated from nuclear power plants was investigated. Single- and bi-solute competitive adsorptions of Co^{2+}, Sr^{2+} and Cs^{+} onto AMP–PAN were investigated. The influencing factors such as co-existing metal ion and surfactants were investigated. Adsorption of Co^{2+}, Sr^{2+} and Cs^{+} onto AMP–PAN occurs via both physical adsorption due to weak van der Waals forces and ion exchange of ammonium molybdophosphate. The results of adsorption model analyses showed that AMP–PAN has high selectivity for Cs^{+}. The maximum adsorption capacities were 0.16, 0.18 and 0.61 mmol/g for Co^{2+}, Sr^{2+} and Cs^{+}, respectively. In bi-solute competitive adsorptions, adsorption of one metal ion was suppressed by the presence of competing metal ion. Alkali metal (Na^{+}) inhibits adsorption of Cs^{+} and the presence of Ca^{2+} ion decreased the adsorption of Co^{2+} onto AMP–PAN. Adsorption behaviors of Co^{2+}, Sr^{2+} and Cs^{+} onto AMP–PAN in the presence of surfactants were quiet different. The presence of cationic (OTMA and HDTMA) and anionic surfactants (SDBS and SOBS) decreased adsorption of Co^{2+}, Sr^{2+} and Cs^{+} onto AMP–PAN, but that of non-ionic surfactants (Tween 80 and Triton X-100) did not.

1. Introduction

Increased operation of nuclear power plants and nuclear laboratories are the source of radioactive wastes released into the environment [1]. Enormous amounts of low-level liquid radioactive waste (LLRW) are being produced as a result of operation, repair and disposal at those facilities. All of these LLRW were composed of different chemical and radiochemical compositions. Therefore, cost-effective volume reduction of LLRW has become of great concern in recent decades. Among the LLRW, laundry wastewater is generated from decontaminating polluted instruments, worker's cloths and taking shower after work [2].

Laundry wastewater is often not compatible with other nuclear facility waste streams and thus it should be treated separately. Laundry wastewater from nuclear power plants in Korea contains radioisotopes, surfactants, background electrolytes, and also suspended and dissolved solids. In particular, it is generally known that surfactants included in laundry wastewater affect the adsorptive removal of radionuclides.

Several technologies such as thermal treatment, precipitation, extraction, membrane, adsorption, and ion exchange have been proposed to treat low-level liquid radioactive wastes [3,4]. Among these techniques, ion exchange is one of the most promising process and many types of inorganic ion exchange materials and adsorbents have been applied [5] including magnetite [3], natural zeolite [4], silicotitanate [6], hexacyanoferrate complexes [7], AMP–calcium alginate composite [8], and PAN-based adsorbers [9–13].

Among the previously developed adsorbents, ammonium molybdophosphate (AMP) is well known to have high Cs selectivity and adsorption capacity [14]. AMP–PAN was developed by Sebesta and others [9,12] combining ammonium molybdophosphate (AMP) with polyacrylonitrile (PAN). Several researchers have demonstrated that AMP–PAN is an effective adsorbent for removing ^{137}Cs from acidic and high salted radioactive waste stream through both batch and dynamic column tests [9–13]. Tranter et al. [11] reported that the AMP–PAN maintained high Cs ion exchange capacity (32 g Cs/kg adsorbent) with high flow rates of heavily salted feed solutions in the bench scale column tests. Todd et al. [12] reported batch equilibrium data for AMP–PAN in simulated INEEL (Idaho National Engineering and Environmental Laboratory, USA) composite tank waste solutions. Cesium adsorption followed the classical Langmuir isotherm and the presence of potassium reduced the distribution coefficient (K_d) to the greatest extent.

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Nomenclature

b_L	Langmuir model constant (L/mmol)
$b_{L,i}$	Langmuir model constant of a solute i in single-solute adsorption (L/mmol)
$b^*_{L,i}$	Langmuir model constant of a solute i in bi-solute competitive adsorption (L/mmol)
C	aqueous-phase equilibrium concentration (mmol/L)
C_0	initial concentration of metal in aqueous solution (mmol/L)
$C_{m,i}$	aqueous-phase equilibrium concentration of a solute i in multi-solute competitive adsorption (mmol/L)
CLM	competitive Langmuir model
E	mean free energy (J/mol) in Dubinin–Radushkevich model
K_d	distribution coefficient (mL/g)
K_F	Freundlich adsorption coefficient $[(\text{mmol/g})/(\text{mmol/L})^{N_F}]$
N	total number of solutes in a mixture
N_F	exponent in Freundlich model
q	solid-phase equilibrium concentration (mmol/g)
$q_{m,i}$	solid-phase equilibrium concentration of a solute i in multi-solute competitive adsorption (mmol/g)
q_{mD}	maximum adsorption capacity of Dubinin–Radushkevich model (mmol/g)
q_{mL}	maximum adsorption capacity of Langmuir model (mmol/g)
$q_{mL,i}$	maximum adsorption capacity of solute i in single-solute adsorption predicted by Langmuir model (mmol/g)
$q^*_{mL,i}$	maximum adsorption capacity of solute i in bi-solute competitive adsorption predicted by Langmuir model (mmol/g)
R	gas constant, 8.314 (J/mole/K)
R^2	coefficient of determination
SSE	sum of squared errors
T	absolute temperature (K)
V	solution volume (L)
W	adsorbent weight (g)
Greek letters	
β	Dubinin–Radushkevich model parameter (mol^2/J^2)
ε	Polanyi potential (J/mol)

The K_d (mL/g) of Cs in 2 M HNO_3 is very high (>60,000), but that in the solutions containing 0.25 M potassium nitrate decreases to 7150. Dynamic column tests demonstrate that calculated dynamic capacity for cesium was 19.6 mg Cs/g adsorbent, for 20 bed volume per hour flows.

However, studies on the AMP–PAN are limited to the treatment of acidic and high salted waste streams from nuclear power plants and application on the treatment of laundry wastewater was not investigated. In this study, we applied AMP–PAN to decontaminate nuclear laundry wastewater that includes salts, surfactants, and suspended and dissolved solids. The objective of this study is to determine the applicability of AMP–PAN to remove radioactive Co^{2+}, Sr^{2+} and Cs^+ in laundry wastewater with widely different chemical compositions. Single- and bi-solute adsorptions of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–PAN were investigated using a batch-type adsorber. Single-solute adsorption data were analyzed using the Freundlich, Langmuir and D–R isotherms. Bi-solute competitive adsorption data were compared with the predictions from competitive Langmuir model (CLM). Effects of Na^+ and Ca^{2+} ions and surfactants on the distribution coefficients (K_d) of Co^{2+}, Sr^{2+} and Cs^+ were also investigated.

2. Materials and methods

2.1. Chemicals

Triammonium 12-molybdophosphate trihydrate (AMP, $(NH_4)_3[PMo_{12}O_{36}]\cdot 3H_2O$, 98%+, Wako Pure Chemical Industries, Ltd., Japan), dimethyl sulfoxide (DMSO, $(CH_3)_2SO$, 99%+, Junsei Chemical Co., Ltd., Japan) and PAN (polyacrylonitrile, MW = 150,000, Sigma–Aldrich Chemical Co., Seoul, Korea) were used to synthesize AMP–PAN. $Co(NO_3)_2\cdot 6H_2O$ (98 + %), $Sr(NO_3)_2$ (99 + %) and $CsNO_3$ (99%) were purchased from Sigma–Aldrich Chemical Co. (Seoul, Korea). The stock solutions of Sr^{2+}, Co^{2+} and Cs^+ were prepared by dissolving $Sr(NO_3)_2$, $Co(NO_3)_2$ and $CsNO_3$ in distilled and deionized water prepared by Barnstead E-pure Water Purification Systems (18.3 MΩ cm, Barnstead, D4641, USA). MES buffer (2-[*N*-morpholino]ethanesulfonic acid hydrate, ACROS Organics, USA) was used to adjust solution pH in adsorption experiments. Na^+ and Ca^{2+} were introduced as $NaNO_3$ (Sigma–Aldrich Chemical Co., Seoul, Korea) and $Ca(NO_3)_2\cdot 4H_2O$ (Sigma–Aldrich Chemical Co., Seoul, Korea). Non-ionic surfactants; Tween 80 (Reidal-de-Haen, Germany) and Triton X-100 (Aldrich, Chemical Co., Korea), anionic surfactants; SOBS (sodium 4-*n*-octylbenzenesulfonate, $C_{14}H_{21}NaO_3S$, TCI, Japan) and SDBS (dodecylbenzenesulfonic acid, sodium salt, $C_{18}H_{29}NaO_3S$, Aldrich Chemical Co., Korea), and cationic surfactants; OTMA (*n*-octyltrimethlammonium chloride, $C_{11}H_{26}ClN$, TCI, Japan) and HDTMA (hexadecyltrimethylammonium chloride, $C_{19}H_{42}NCl$, Sigma–Aldrich Chemical Co., Seoul, Korea) were used as model surfactants. All reagents were of analytical grade and were used without further purification.

2.2. Adsorbent preparation

AMP–PAN (ammonium molybdophosphate–polyacrylonitrile) was synthesized following the procedure reported by Moon et al. [10]. The synthesized AMP–PAN was composed of 70 wt.% of AMP loaded on a PAN support. Triammonium 12-molybdophosphate trihydrate (AMP, $(NH_4)_3[PMo_{12}O_{36}]\cdot 3H_2O$) was used to prepare the inorganic active ion exchangers. 20 g of AMP and 0.8 g of Tween 80 were combined with 100 mL of dimethyl sulfoxide (DMSO). After stirring the solution for 1 h at 50 °C and 250 rpm, 8 g of PAN was added to this solution and then stirred using a mechanical agitator for 5 h at 50 °C and 250 rpm to obtain a homogeneous solution. The composite mixture was fed into a dual nozzle to obtain the spherical composite beads. The AMP–PAN beads were washed three times with distilled and deionized water and then dried in an oven for 24 h at 60 °C.

2.3. Adsorption experiment

Batch adsorption experiments of cobalt, strontium and cesium were conducted in 15 mL conical tubes (Polypropylene, SPL Co., Korea) containing 0.5 g of AMP–PAN for cobalt and strontium and 0.2 g of AMP–PAN for cesium, respectively. To investigate the effect of pH on adsorption, pH values were adjusted to 2–10 using 0.1N HNO_3 and 0.1N NaOH. The vials containing 0.1 g of AMP–PAN were filled with approximately 15 mL of 10 mM of Co, Sr and Cs solutions at different pHs. To determine the effect of pH on metal precipitation, the pH values of adsorbent-free metal solutions were adjusted in the same manner and filtered through 0.2 μm syringe filter (Whatman, cellulose nitrate membrane filter, ϕ = 25 mm). The aqueous-phase concentrations of Co^{2+}, Sr^{2+} and Cs^+ were determined by inductively coupled plasma optical emission spectrometry (ICP-OES, Optima 2100 DV, Perkin-Elmer Co., USA).

Table 1
Lists of the name, structural formula, and most commonly used abbreviation and CMC of the applied surfactants used.

Type		Surfactants name	Formula	Molecular weight	Abbreviation	CMC (mM)	Concentrations (mM)		Refs.
							Below CMC	Above CMC	
Non-ionic	Short chain	Triton X-100	$C_{14}H_{22}O(C_2H_4O)_n$ $n = 9–10$	625	Triton X-100	0.24	0.1	1.0	[17]
	Long chain	Polysorbate 80	$C_{64}H_{124}O_{26}$	1310	Tween 80	0.012	0.007	0.153	[18]
Cationic	Short chain	*n*-Octyltrimethlammonium chloride	$C_{11}H_{26}NCl$	207.78	OTMA	140	0.5	150	[19]
	Long chain	Hexadecyltrimethylammonium chloride	$C_{19}H_{42}NCl$	364.5	HDTMA	1.3	0.5	50	[20]
Anionic	Short chain	Sodium octylbenzenesulfonate	$C_{14}H_{21}NaO_3S$	294.39	SOBS	10	0.5	15	[21]
	Long chain	Dodecylbenzenesulfonic acid, sodium salt	$C_{18}H_{29}NaO_3S$	348.48	SDBS	25	0.5	50	[22]

To obtain adsorption isotherms, different initial concentrations (1, 2, 5, 10, 15 and 20 or 30 mM) of each metal solution were used. The pH values of the solutions were maintained at 5 using 0.05 M MES buffer. Preliminary experiments showed that the buffer has no effect on metal adsorption. Other researchers also reported that no detectable complexation reactions occur between metals and MES buffer [15]. The solution pH was controlled to prevent the formation of metal hydroxides and carbonates. Molar distributions of cobalt, strontium and cesium species at all pH ranges were predicted using the program of MINEQL$^+$ version 4.0 for Windows (Environmental Research Software, USA).

After filling the aqueous solution into the vial, the mixture was horizontally mixed on a shaker for 24 h at 20 °C and 200 rpm. After shaking, the mixture was centrifuged for 20 min at 3000 rpm and filtered through the membrane filter. The aqueous-phase concentrations of Co^{2+}, Sr^{2+} and Cs^+ were determined by the ICP-OES. The concentrations of Cs^+ were analyzed using standard addition methods [16]. The solid-phase equilibrium concentrations were calculated by assuming all concentration changes in solution phase result from adsorption onto the solid phase. All experiments were run in duplicate. The equilibrium pH was determined by a pH meter (Orion, Model 720, Thermo Electron Corp., USA).

Bi-solute systems (Sr^{2+}/Co^{2+}, Sr^{2+}/Cs^+, and Co^{2+}/Cs^+) were prepared by mixing each metal solution of the same molar concentration in a 1:1 volume ratio for each solute. Bi-solute competitive adsorption experiments were conducted in the same manner as were in the single-solute adsorption experiments. The equilibrium concentrations in the mixture were also determined using the ICP-OES.

2.4. Effect of co-existing ions on adsorption

The effects of co-existing cations (Na^+ and Ca^{2+}) on the adsorption of Sr, Co and Cs were investigated. The initial concentration of Co^{2+}, Sr^{2+} and Cs^+ was 10 mM, while the concentrations of co-existing ions (Na^+ and Ca^{2+}) were maintained at 0.2, 2 and 20 mM. After conducting adsorption experiments as were in the single-solute adsorptions, the aqueous-phase concentrations of Na^+ and Ca^{2+} were determined by the ICP-OES. The distribution coefficient (K_d) was conducted to evaluate the effects of co-existing cations.

$$K_d = \frac{C_0 - C}{C}\frac{V}{W} \tag{1}$$

where C_0 is the initial concentration (mmol/L) of Co^{2+}, Sr^{2+} and Cs^+ in each solution, C is the aqueous-phase equilibrium concentration (mmol/L), V is solution volume (mL), and W represents the mass of adsorbent (g). The distribution coefficient (K_d, mL/g) represents the concentration of cation exchanged onto the solid, versus the concentration left in solution. To ensure accurate comparison of K_d values, several factors such as adsorbents: solution ratio, temperature, solution composition and material pretreatment were considered.

2.5. Effect of surfactants on adsorption

The effects of surfactants on the adsorption of Sr, Co and Cs were also investigated. The applied initial concentration of Co^{2+}, Sr^{2+} and Cs^+ was 10 mM. Three type of surfactants; Triton X-100 and Tween 80 as non-ionic surfactants, and *n*-octyltrimethlammonium chloride (OTMA) and cetyltrimethylammonium chloride (HDTMA) as cationic surfactants, sodium octylbenzenesulfonate (SOBS) and dodecylbenzenesulfonic acid, sodium salt (SDBS) as anionic surfactants were used. The concentrations of the surfactants were applied at below, near and above their critical micelle concentration (CMC). The physicochemical properties of the surfactants were summarized in Table 1. After mixing the surfactant with the metal solutions, adsorption experiments were conducted in the

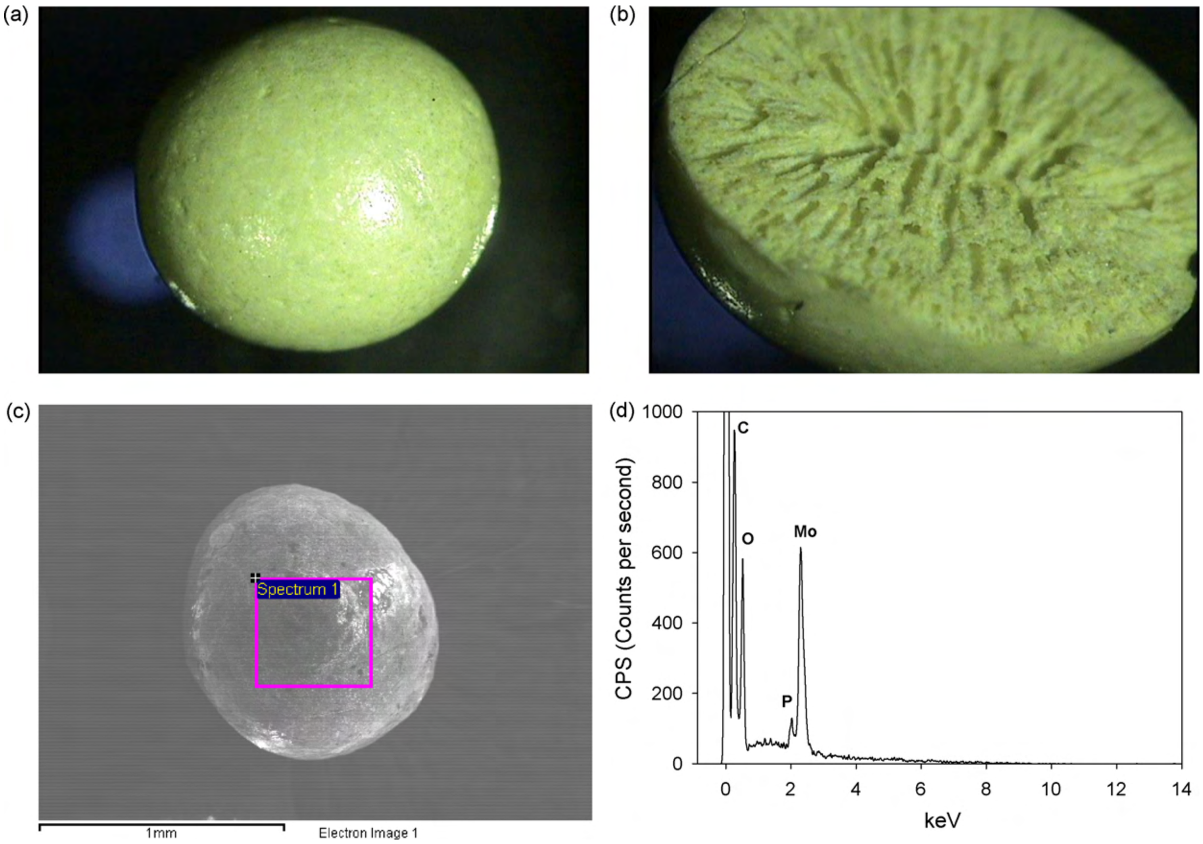

Fig. 1. The image of Video Microscope (VM) (a) ×100 and (b) ×200 magnification, (c) the SEM image and (d) the EDS peaks of AMP–PAN.

same manner as were in the single-solute adsorption experiments. K_d (distribution coefficient) values were calculated to evaluate the effects of surfactants.

2.6. Single-solute adsorption models

The Freundlich model is often used to describe adsorption data:

$$q = K_F C^{N_F} \tag{2}$$

where C (mmol/L) is the aqueous-phase equilibrium concentration, q (mmol/g) is the solid-phase equilibrium concentration, and K_F [(mmol/g)/(mmol/L)^{N_F}] and N_F (−) are the Freundlich adsorption coefficient and the Freundlich exponent, respectively.

The Langmuir model for single-solute adsorption is represented as:

$$q = \frac{q_{mL} b_L C}{1 + b_L C} \tag{3}$$

where q_{mL} (mmol/g) and b_L (L/mmol) are the Langmuir model parameters that represent maximum adsorption capacity and site energy factor, respectively.

The Dubinin–Radushkevich (D–R) isotherm is more general than the Langmuir isotherm because it does not assume a homogeneous surface or constant adsorption potential. It was applied to distinguish between the physical and chemical adsorptions of heavy metals [23].

$$q = q_{mD}\ \exp(-\beta\varepsilon^2) = q_{mD}\ \exp\left[-\beta\left(RT\ \ln\left(1 + \frac{1}{C}\right)\right)^2\right] \tag{4}$$

where β (mol^2/J^2) is a constant related to the mean free energy of adsorption per mole of the adsorbate, q_{mD} (mmol/g) is the theoretical saturation capacity and ε (J/mol) is the Polanyi potential (= $RT\ln(1+1/C)$), where R (J/mol/K) is the gas constant and T (K) is the absolute temperature.

The constant β gives an idea about the mean free energy E (J/mol) of adsorption per molecule of the adsorbate when it is transferred to the surface of the solid from infinity in the solution and can be calculated using the relationship [24].

$$E = \frac{1}{(2\beta)^{1/2}} \tag{5}$$

The adsorption model parameters were determined using a commercial software package, TableCurve 2D® (Version 5.0, SPSS, Inc.).

Table 2
Physicochemical properties of AMP–PAN.

Properties	
Bead diameter (mm)	1–2
BET pore volume (cm^3/g)	0.17
BET pore size (Å)	314.1
BET surface area (m^2/g)	32.69

2.7. Bi-solute competitive adsorption model

The competitive Langmuir model (CLM) was used to analyze bi-solute competitive adsorption behaviors [25]. The CLM is an extended form of the Langmuir model which allows predictions of the amount of a solute i adsorbed per unit weight of an adsorbent,

$q_{m,i}$ in the presence of other solutes.

$$q_{m,i} = \frac{q_{mL,i} b_{L,i} C_{m,i}}{1 + \sum_{j=1}^{N} b_{L,j} C_{m,j}} \qquad (6)$$

where $C_{m,i}$ (mmol/L) is the equilibrium concentration of solute i in a mixture consisting of N solutes, and constants $b_{L,i}$ (L/mmol) and $q_{mL,i}$ (mmol/g) are parameters determined by fitting the Langmuir model to the single-solute adsorption data of solute i.

3. Results and discussion

3.1. Characteristics of AMP–PAN

The physicochemical properties of the AMP–PAN used in this study were summarized in Table 2. The size of AMP–PAN bead was adjusted to 1–2 mm scale for practical use in industry. The surface area of AMP–PAN was 32.69 m^2/g. The image of Video Microscope (VM) and EDS peaks of AMP–PAN was shown in Fig. 1. The EDS peaks of AMP and PAN showed their elemental compositions. The FT-IR spectra of AMP–PAN was shown in Fig. 2. The vibrational bands of P–O, Mo=O, and Mo–O–Mo in the AMP are observed from 1067, 963, and 870 cm^{-1} to 1061, 960 and 867 cm^{-1}, respectively. The peak range of 1400–1500 cm^{-1} is assigned to NH_4^+. The broadness of the O–H stretching band in the region of 3550–3400 cm^{-1} is caused by the H-bonding between the adsorbed H_2O. Maximum adsorption at 2243 cm^{-1} is due to the nitrile groups in the PAN [26–28].

3.2. Effect of pH

The metal speciations of Co, Sr and Cs in solution calculated by MINEQL+ (version 4.5) were shown in Fig. 3. Co^{2+} was the dominant Co species at pH below 7. $Co(OH)_2$ precipitates formed at pH above 7. Sr^{2+} was the dominant species in solution at pH below 11; at pH values above 11, $Sr(OH)^+$ was dominant. However, Cs exists as Cs^+ ion at all pH ranges.

Total uptake (= sorption + precipitation) and precipitation of Co, Sr and Cs onto AMP–PAN as a function of pH were shown in Fig. 4 (C_0 = 10 mM). The total Co uptake increased with pH, with a sharp rise occurring at pH above 8. The total Co uptake at pH < 8 was mainly attributed to sorption onto the surface of AMP–PAN, but precipitation was the major uptake mechanism at pH > 8. The total Sr uptake also increased with pH followed by sharp increase at pH > 6.5. At acidic pH ranges, the metal ion removal was inhibited due to the presence of H^+ ions that compete with the Sr^{2+} ions for the adsorption sites [4]. However, the effect of pH on total Cs uptake was quite different; metal uptake was nearly constant at all pH ranges. This is because Cs exists as Cs^+ at all pH ranges as predicted by MINEQL+ (Fig. 3). The constant total Cs^+ uptake is attributed to the ion exchange between NH_4^+ in AMP and Cs^+ and adsorption of Cs^+ onto the macropores in the AMP–PAN beads [29].

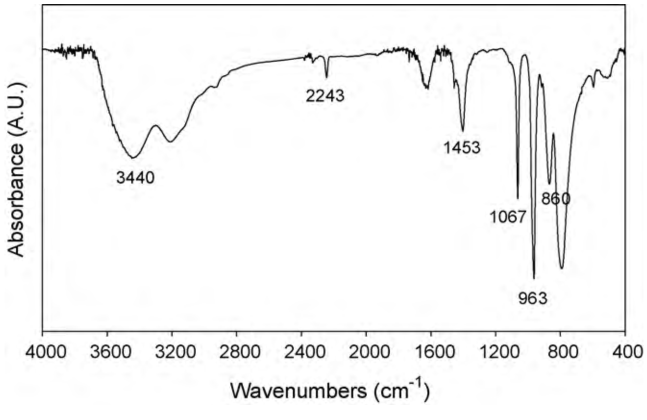

Fig. 2. FT-IR analysis of AMP–PAN used in this study.

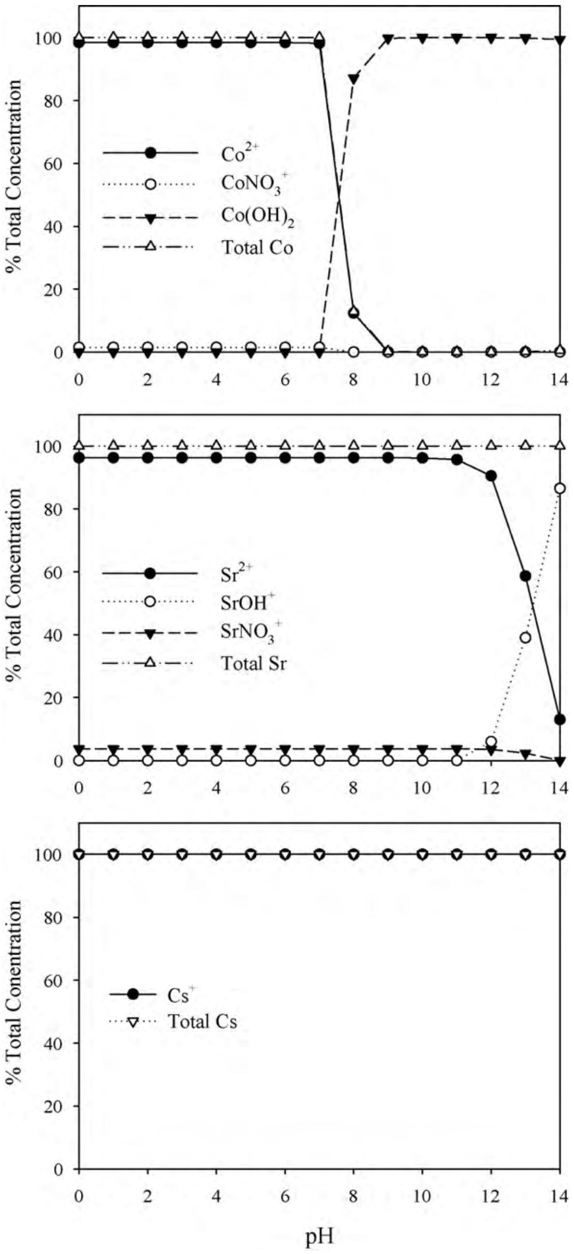

Fig. 3. The distributions of cobalt, strontium and cesium species as a function of pH predicted by MINEQL+ version 4.0.

3.3. Single-solute adsorption

As shown in Fig. 5, single-solute adsorptions of Co, Sr and Cs onto AMP–PAN were conducted at pH 5. The solution pH was controlled to prevent the formation of metal hydroxides and carbonates over at pH 5. At the pH condition, all metals exist in the ionic state as shown by the metal speciation of MINEQL+ (Fig. 3). The Freundlich, Langmuir and D–R models were fitted to the adsorption data by using the non-linear regression method (Fig. 5 and Table 3).

The Freundlich model fitted the experimental data well ($0.96 < R^2 < 0.99$). The Freundlich adsorption constant, K_F, indicat-

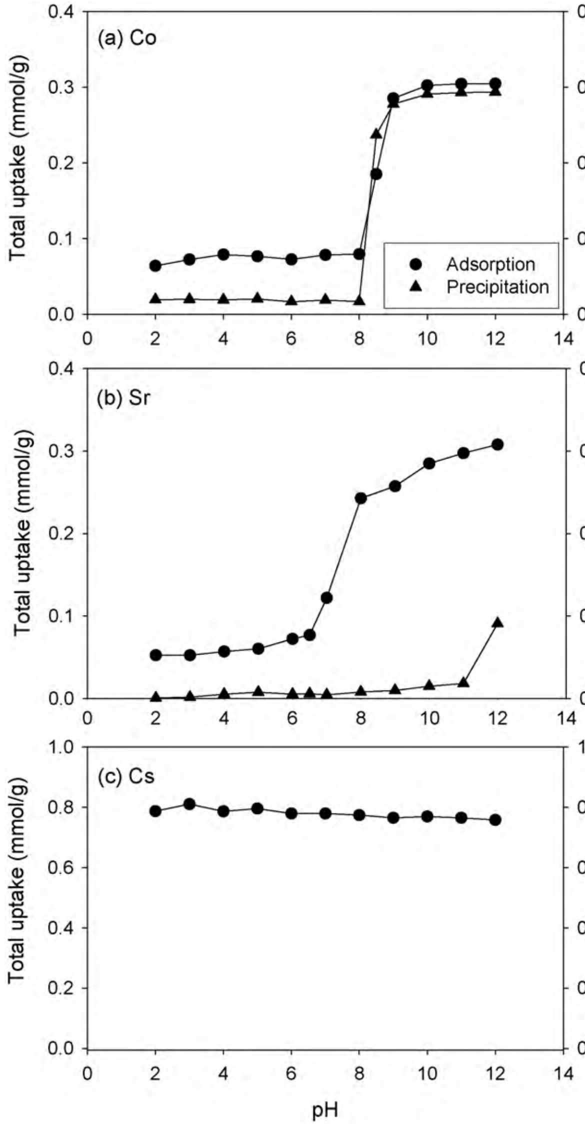

Fig. 4. Effect of pH on the adsorption of (a) Co, (b) Sr and (c) Cs onto AMP–PAN.

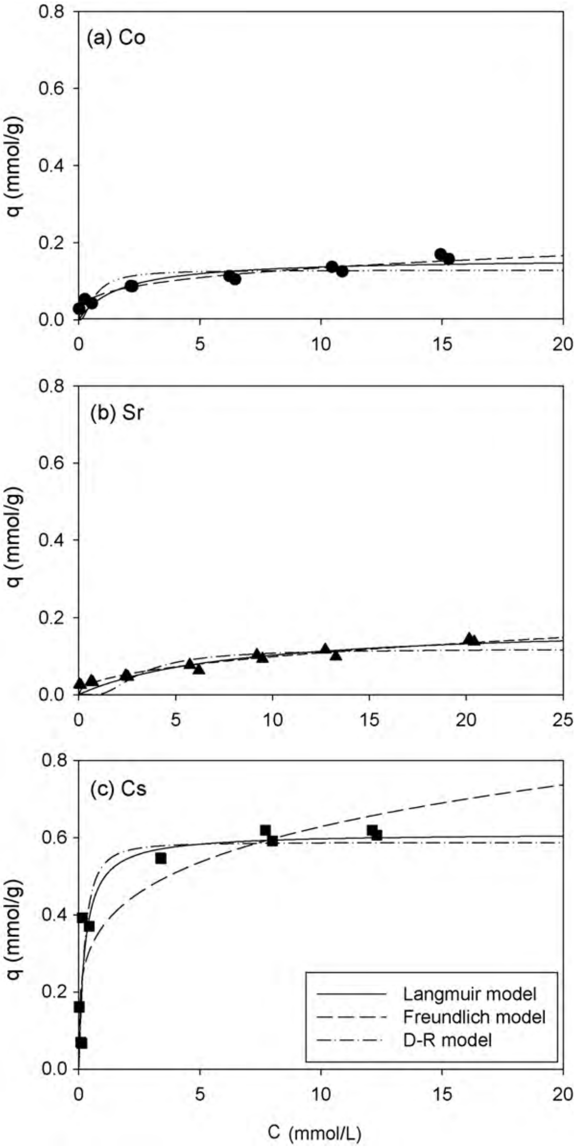

Fig. 5. Single-solute adsorption of (a) Co, (b) Sr and (c) Cs onto AMP–PAN at pH 5.

ing the adsorption capacity of the adsorbent was in the order of Cs ≫ Co > Sr. The Freundlich exponent, N_F, is a measure of the deviation from linearity of the adsorption. If a value for N_F is equal to unity, the adsorption is linear. If N_F value is above 1, this implies that

Table 3
Freundlich, Langmuir and Dubinin–Radushkevich model parameters for single-solute adsorption of Co, Sr and Cs at pH 5.

Freundlich model					
Solute	K_F [(mmol/g)/(mmol/L)^{N_F}]	N_F (−)	R^2	SEE	
Co	0.0677 ± 0.0046	0.2998 ± 0.0299	0.9917	0.0105	
Sr	0.0352 ± 0.0040	0.4469 ± 0.0453	0.9875	0.0102	
Cs	0.3707 ± 0.0326	0.2295 ± 0.0414	0.9646	0.0929	
Langmuir model					
Solute	q_{mL} (mmol/g)	b_L (L/mmol)	R^2	SEE	R_L*
Co	0.1601 ± 0.0164	0.5926 ± 0.2641	0.9684	0.0206	0.0778
Sr	0.1845 ± 0.0301	0.1250 ± 0.0482	0.9723	0.0152	0.2857
Cs	0.6118 ± 0.0420	4.1162 ± 1.5204	0.9659	0.0911	0.0120
Dubinin–Radushkevich model					
Solute	q_{mD} (mmol/g)	β (mmol^2/J^2 × 10^{-8})	R^2	SEE	E (kJ/mol)
Co	0.1287 ± 0.0109	14.10 ± 7.49	0.9407	0.0282	1.88
Sr	0.1183 ± 0.0109	170.35 ± 67.48	0.9331	0.0236	0.54
Cs	0.5878 ± 0.0405	3.64 ± 1.18	0.9565	0.0992	3.71

* Calculated at C_0 = 20 mM.

adsorption process is chemical, but if N_F value is below 1, adsorption is favorable for a physical process [30]. The N_F values at equilibrium ranged from 0.22 to 0.45, represents non-linear and favorable physical adsorption.

The Langmuir model also fitted the experimental data well ($0.96 < R^2 < 0.97$). The q_{mL} value was in the order of Cs ≫ Co > Sr. The q_{mL} value for Cs, 0.61 mmol Cs/g AMP–PAN (= 81 mg Cs/g AMP–PAN), was in good agreement with that of previous study by others [6]. Todd and Romanovskiy reported q_{mL} value of 85 mg Cs/g AMP–PAN for simulated composite INEEL tank waste [6]. The essential characteristic of Langmuir isotherm can be expressed in terms of a dimensionless constant, separation factor R_L (–), that describe the type of isotherm [31]:

$$R_L = \frac{1}{1 + b_L C_0} \tag{7}$$

where b_L (L/mmol) is the Langmuir constant and C_0 (mmol/L) is the initial concentration of metal solution. The values of R_L indicate the type of isotherm to be unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) or irreversible ($R_L = 0$). The R_L values calculated at $C_0 = 20$ mM were between 0.01 and 0.29 (Table 3), indicating that adsorptions of all heavy metals onto AMP–PAN are highly favorable.

The Dubinin–Radushkevich (D–R) model was also fitted to the single-solute adsorption data. The D–R model fitted the data well ($0.93 < R^2 < 0.95$). The q_{mD} value of the D–R model increased in the order of Cs ≫ Co > Sr. The q_{mD} values of D–R model were nearly same as the q_{mL} values for the Langmuir isotherm (Table 3). The value of mean free energy E in D–R model gives information whether the adsorption mechanism is ion exchange or physical adsorption. If the magnitude of E is between 8 and 16 kJ/mol, the adsorption process follows ion exchange, while for the values of $E < 8$ kJ/mol, the adsorption process is of a physical nature. For the values of $E > 16$ kJ/mol, the adsorption occurs via chemical adsorption [24]. In this study, the E values calculated using Eq. (5) were less than 8 kJ/mol indicating that adsorption of Co, Sr and Cs onto AMP–PAN occurred via physical adsorption due to weak van der Waals forces [32]. However, the major mechanism of the adsorption of Co, Sr and Cs onto AMP–PAN could be ion exchange. For the initial aqueous metal concentrations of 5 mM, the solid-phase equilibrium concentrations of Co, Sr and Cs were 0.19, 0.24 and 0.79 meq/g, respectively. The aqueous-phase equilibrium NH_4^+ concentrations leached from AMP–PAN were 0.12, 0.14 and 0.44 meq/g, respectively. The aqueous-phase equilibrium concentrations of NH_4^+ ion-exchanged from AMP–PAN were lower than the solid-phase equilibrium concentrations of metals. This explains that ion exchange contributes 56–63% of the total adsorption of the metals. Therefore both ion exchange and physical adsorption would be involved in adsorption. In conclusion, the mean free energy (E) in the D–R model cannot clearly explain the adsorption mechanism.

The isotherm model analysis showed that AMP–PAN had relatively higher selectivity for Cs than for Co and Sr. The higher selectivity of Cs can be explained by the ion exchange mechanism of ammonium molybdophosphate (AMP) [33]. The adsorption mechanism is explained via a simple reaction of the initial counter-ions on the phosphomolybdate (ammonium) for cesium cation, with subsequent release of the free ammonium ions as shown in below Eq. (8) [29].

$$\begin{aligned}(NH_4)_3PMo_{12}O_{40} + x\mathrm{Cs}^+(aq) &\rightarrow \mathrm{Cs}_x(NH_4)_{3-x}PMo_{12}O_{40} \\ &+ x(NH_4)^+(aq)\end{aligned} \tag{8}$$

According to Smit and Van [14], 'the phosphomolybdate complex ion, $(PMo_{12}O_{40})^{3-}$, consists of a hollow sphere formed by the 12 MoO_6 octahedra with the PO_4 group in the center of the crystal structure of the ammonium salt of this ion. The ammonium ions associated with water molecules are probably fitted in between these spheres of negative ions thus accounting for the cohesion of these ions. They also reported that for the exchange of NH_4^+ with the monovalent ions (Na^+, K^+, Rb^+ and Cs^+), Cs^+ is preferred to the others. However, Co^{2+} and Sr^{2+} adsorption onto AMP–PAN were less than Cs^+ adsorption although they are the divalent ions. It was reported that AMP–PAN is more selective for removing monovalent alkali metal ions than divalent metal ions [34].

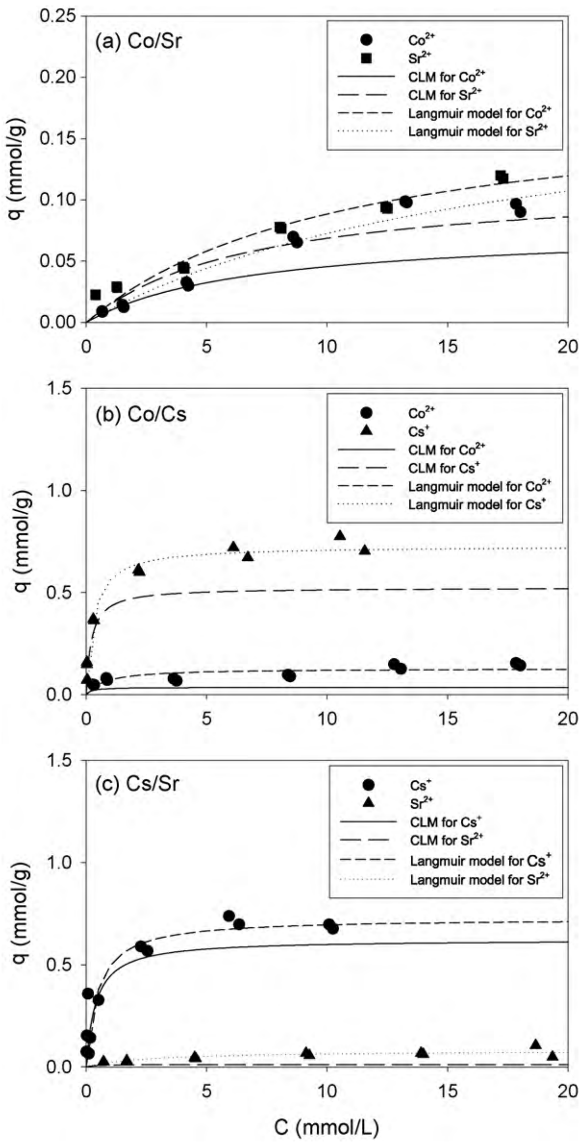

Fig. 6. Bi-solute competitive adsorption of (a) Co/Sr, (b) Co/Cs and (c) Cs/Sr at pH 5. Lines represent CLM predictions.

3.4. Bi-solute competitive adsorption

Bi-solute competitive adsorptions of Co/Sr, Co/Cs and Cs/Sr onto AMP–PAN were analyzed by the Langmuir model (Fig. 6 and Table 4). The effect of simultaneously existed competing metal on the adsorption of the metal on AMP–PAN was evaluated by the ratio of the adsorption capacity of the metal ion in single- ($q_{mL,i}$) and bi-solute ($q^*_{mL,i}$) competitive adsorptions (Table 5). The $q^*_{mL,i}/q_{mL,i}$ is the ratio of the adsorption capacity of one metal in the bi-solute system to that of the metal in the single-solute system. When the ratio is greater than 1, the adsorption is accelerated in the bi-solute system. There is no influence when the ratio is equal to 1. When the

Table 4
Langmuir model parameters for bi-solute competitive adsorption of Co, Sr and Cs at pH 5.

Compound	Solute	q^*_{mL} (mmol/g)	b^*_L (L/mmol)	R^2	SEE
Cobalt	Co/Sr	0.2041 ± 0.0441	0.0553 ± 0.0203	0.9878	0.0077
	Co/Cs	0.1282 ± 0.0121	1.3011 ± 0.6406	0.9525	0.0246
Strontium	Sr/Co	0.1847 ± 0.0303	0.0922 ± 0.0306	0.9863	0.0094
	Sr/Cs	0.0804 ± 0.0120	0.3581 ± 0.1925	0.9428	0.0143
Cesium	Cs/Co	0.7285 ± 0.0270	3.3277 ± 0.6797	0.9911	0.0528
	Cs/Sr	0.7267 ± 0.0573	2.1405 ± 0.8946	0.9657	0.1003

Table 5
Comparison of q_{mL} and b_L values of single-solute and bi-solute competitive adsorption.

Binary system (1)/(2)[a]	$(q_{mL,1}/q_{mL,2})$[b]	$(q^*_{mL,1}/q^*_{mL,2})$[c]	$(q^*_{mL,1}/q_{mL,1})$	$(q^*_{mL,2}/q_{mL,2})$
Co/Sr	0.865	1.103	1.156	1.000
Co/Cs	0.261	0.176	0.800	1.191
Sr/Cs	0.302	0.110	0.432	1.188
Binary system (1)/(2)[a]	$(b_{L,1}/b_{L,2})$[b]	$(b^*_{L,1}/b^*_{L,2})$[c]	$(b^*_{L,1}/b_{L,1})$	$(b^*_{L,2}/b_{L,2})$
Co/Sr	4.744	0.598	0.093	0.736
Co/Cs	0.144	0.391	2.194	0.809
Sr/Cs	0.030	0.167	2.864	0.520

[a] The metal ions in binary system in the order of (1) and (2).
[b] q_{mL} and b_L denote Langmuir model parameters for single-solute adsorption.
[c] q^*_{mL} and b^*_L denote Langmuir model parameters for bi-solute competitive adsorption.

ratio is less than 1, the adsorption of one metal is hindered by the existence of the other metal in binary system. As expected, when either Co or Sr competes with Cs for adsorption in the bi-solute systems, the ratio of $q^*_{mL,Cs}/q_{mL,Cs}$ was greater than unity and the ratio of both $q^*_{mL,Co}/q_{mL,Co}$ and $q^*_{mL,Sr}/q_{mL,Sr}$ was less than unity. This explains that the Cs adsorption was promoted while Co or Sr adsorption was suppressed. When Co competed with Sr for adsorption in the bi-solute system, the ratio $q^*_{mL,Co}/q_{mL,Co}$ was greater than unity and the ratio of $q^*_{mL,Sr}/q_{mL,Sr}$ was equal to unity. This indicates that the Co adsorption was promoted while the Sr adsorption was restrained in the bi-solute system.

In the bi-solute systems, the interactions between two solutes may mutually enhance or mutually inhibit adsorption capacity [35]. In general, a mixture of different adsorbates may exhibit three possible types of behaviours: synergism, antagonism and non-interaction [25]. Factors that affect the adsorption preference of an adsorbent for different kinds of adsorbates may be related to the characteristics of the binding sites (e.g., functional groups, structure, surface properties, etc.), the properties of the adsorbates (e.g., concentration, ionic size, ionic weight, molecular structure, ionic nature or standard reduction potential, etc.) and solution chemistry (e.g., pH, ionic strength, etc.) [36]. Currently, it is difficult to determine which factors affect the preference of Cs adsorption onto AMP–PAN. For that reason, the observed results may result from a combination of all the above factors [37] and thus they are subjected to further investigation.

The binding energy coefficient ($b_{L,i}$ for single-solute adsorption and $b^*_{L,i}$ for bi-solute competitive adsorption, respectively) varied with metal solution. AMP–PAN showed higher affinity for Cs than Sr or Co, in both single- ($b_{L,\mathrm{Cs}} \gg b_{L,\mathrm{Co}} > b_{L,\mathrm{Sr}}$) and bi-solute ($b^*_{L,\mathrm{Cs/Co}} \gg b^*_{L,\mathrm{Co/Cs}} > b^*_{L,\mathrm{Sr/Cs}}$) adsorptions. The b^*_L value of Cs ($b^*_{L,\mathrm{Cs}}$) in bi-solute competitive adsorption was less than that of single-solute adsorption ($b_{L,\mathrm{Cs}}$). The maximum adsorption capacity values of Cs in bi-solute competitive adsorption ($q^*_{mL,\mathrm{Cs}}$) were higher than that in the single-solute adsorption ($q_{mL,\mathrm{Cs}}$). This is because competition for adsorption sites suppresses the retention of cesium on more specific sorption positions and the metal ions are adsorbed more weakly. While binding strength or affinity constant (b), estimates made from adsorption isotherms should only be considered qualitatively [38], they have been related to the free energy change of adsorption of different species. Higher b values have been related to specifically adsorbed metals at high-energy surfaces with low dissociation constants. Alternatively, lower b values appear to be related to adsorption at low energy surfaces with high dissociation constants [39–41].

Table 6
R^2 and SSE values for bi-solute competitive adsorption predictions from competitive Langmuir model (CLM).

Bi-solute system	Compound	R^2	SEE
Co/Sr	Co	0.8204	0.0044
	Sr	0.9306	0.0022
Co/Cs	Co	0.5081	0.0315
	Cs	0.9239	0.1202
Cs/Sr	Cs	0.9495	0.0743
	Sr	0.3261	0.0122

The CLM predictions for competitive adsorptions of Co/Sr, Co/Cs and Cs/Sr at pH 5 were shown in Fig. 6. To compare predictions with the experimental data, R^2 and the sum of squared error (SSE) from the following equations were also calculated and listed in Table 6. In the equation, $\tilde{q}_i$ denotes the adsorption of a solute predicted by Langmuir model. The predictions were successful in most of the adsorptions ($R^2 > 0.82$) except Co in Co/Cs ($R^2 = 0.51$) and Sr in Cs/Sr ($R^2 = 0.33$).

$$R^2 = \frac{\sum q_i^2 - \mathrm{SSE}}{\sum q_i^2} \tag{9}$$

$$\mathrm{SSE} = \sum (q_i - \tilde{q}_i) \tag{10}$$

3.5. *Effect of co-existing cations on adsorption*

The metal adsorption depends on the adsorbent characteristics, compositions of liquid solution, characteristics of the involved metals, and their competition for adsorption sites on adsorbents. Hence, the effect of co-existing cations (Na^+ and Ca^{2+}) on the adsorption was investigated. The influence of co-existing ion (0.2 mM of Na^+ or Ca^{2+}) on the adsorptions of Co^{2+}, Sr^{2+} and Cs^+ (10 mM) was negligible because the Na^+ or Ca^{2+} concentration was too low to affect the adsorption of metals on AMP–PAN (data not shown). However,

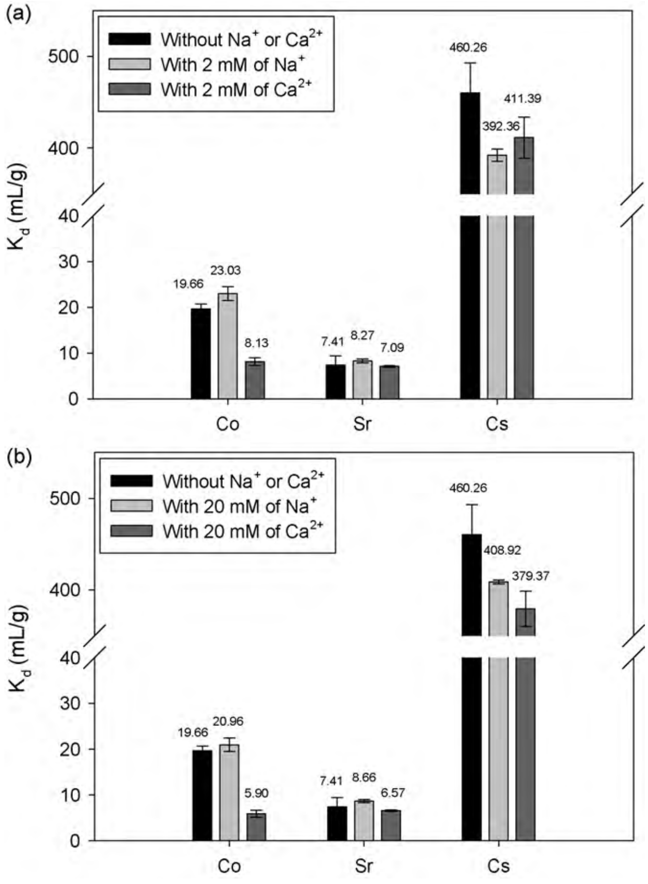

Fig. 7. The distribution coefficient (K_d) values of Co, Sr and Cs in the stock solution including co-existing ions for 24 h at 25 °C. (a) Na^+ or Ca^{2+} = 2 mM and (b) Na^+ or Ca^{2+} = 20 mM, $Co^{2+}/Sr^{2+}/Cs^+$ = 10 mM, V/m = 30 mL/g for Co^{2+} and Sr^{2+}, and 75 mL/g for Cs^+.

the influence of 2 and 20 mM of Na^+ or Ca^{2+} on the adsorption of Co^{2+}, Sr^{2+} and Cs^+ on AMP–PAN was quite different (Fig. 7).

The distribution coefficients (K_d) showed that the presence of 2 and 20 mM of Na^+ decreased the Cs^+ adsorption onto AMP–PAN. The Cs^{2+} adsorption was decreased up to 85–89% compared to the Cs^+ adsorption without cations. Smit and Van [14] demonstrated that a selectivity sequence for the alkali metals is similar to other heteropoly acids of the Keggin structure: $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$. The alkali metals (i.e. Cs^+ and Na^+) competed for the same site in the AMP–PAN to exchange $NH_4{}^+$. The presence of 2 and 20 mM of Ca^{2+} also decreased the K_d of Cs^+. Cations adsorbed onto AMP are stripped of their hydration water upon entering the lattice due to the anhydrous nature of AMP [42]. The selectivity of AMP is partially a function of the size of the anhydrous form of the counter ion [43]. The ionic radii of metals are the influential factors determining the adsorption affinity onto AMP–PAN. The ionic radii of Cs^+ (1.69 Å) and $NH_4{}^+$ (1.48 Å) are similar making ion exchange between these ions possible. However, the ionic radius of Ca^{2+} (0.99 Å) is much smaller than that of Cs^+, which slightly inhibited the adsorption of Cs^+ onto AMP–PAN [44]. The K_d of Sr^{2+} was not changing in the presence of 2 or 20 mM of Na^+ and Ca^{2+}. The presence of Na^+ also had no effect on the adsorption of Co^{2+} onto AMP–PAN. However, the presence of 2 and 20 mM of Ca^{2+} decreased the K_d of Co^{2+} onto AMP–PAN. This is because Ca^{2+} competes with Co^{2+} for the same adsorption site on the AMP–PAN, while Na^+ does not. Coetzee and Vanwyk [45] carried out bivalent cation exchange studies on AMP. In their results, a little amount of NH_4 exchanged with divalent cations and the maximum exchange capacity with NH_4 is related to the ionic radii of the ions. The maximum $NH_4{}^+$ ion exchange capacity was in the order of Sr^{2+} (34.5%, 1.13 Å) > Ca^{2+} (32.9%, 0.99 Å) > Co^{2+} (23.5%, 0.72 Å) consistent with the ionic radii [44]. The effect of the co-existing cations on the adsorption onto AMP–PAN is highly complicated because the affinity of AMP to exchange a given cation is a function of ion size, charge, and the relative insolubility of the heteropoly acid (HPA) salt of a particular count ion [43].

3.6. Effect of surfactants on adsorption

The earlier study showed that AMP–PAN is a suitable adsorption material for the treatment of radioactive wastewater [11]. However, the effect of surfactants present in radioactive laundry wastewater on the adsorption of metal ions onto AMP–PAN was not fully investigated. Detergents to clean the worker's body and protective clothes include a various kinds of surfactants. Therefore, the effect of surfactant types, the chain length, and the concentrations on the adsorptive removal of the metals onto AMP–PAN were investigated (Fig. 8).

Adsorption behaviors of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–PAN in the presence of three different types of surfactants were widely different. For non-ionic surfactants, Triton X-100 had no effect on the adsorption of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–PAN (Fig. 8a). The K_d values of Tween 80 were similar to control K_d values (i.e. without surfactants) of Co^{2+}, Sr^{2+} and Cs^+ in most cases except two; the K_d value of Cs^+ increased at below CMC, while that of Co^{2+} decreased at above CMC of Tween 80 (Fig. 8b).

Cationic surfactants directly affected the adsorption of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–APN (Fig. 8c and d). As OTMA concentration increased to near and above CMC, the K_d values of Co^{2+}, Sr^{2+} and Cs^+ decreased. In contrast, the K_d values of Co^{2+}, Sr^{2+} and Cs^+ increased at OTMA concentration below CMC. In the presence of HDTMA at above CMC, the K_d values of Co^{2+} and Sr^{2+} were hardly changed. In contrast, the presence of HDTMA at all concentration level, the K_d values of Cs^+ decreased. In particular, the K_d value of Cs^+ was highly decreasing at above CMC of HDTMA. Lee et al. [46] reported that the adsorption of lead gradually decreased as the mass of HDTMA adsorbed by the bentonite increased, in agreement with our results.

The presence of anionic surfactants highly affected the adsorption of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–PAN (Fig. 8e and f). When SOBS or SDBS was present in the metal solutions, the adsorptions of Co^{2+} and Sr^{2+} sharply increased except Co^{2+} adsorption under the presence of SDBS. Anionic surfactant molecules, which are negatively charged, can bind with positively charged metal ions and thus the formation of cation–SDBS or –SOBS complex can occur in the solution [47]. When SDBS was present in Co^{2+} solution, the adsorption of Co^{2+} on the accessible adsorption sites of AMP–PAN surfaces may be inhibited due to the formation of Co^{2+}–SDBS complex. A similar mechanism has been proposed for cationic surfactant and chromate adsorption to natural clinoptilolite [47]. When the SOBS or SDBS concentration was near and above CMC, the adsorption of Cs^+ onto AMP–PAN decreased. This is because SOBS or SDBS does not make complexes with Cs^+, but the formed SOBS or SDBS micelles may compete with Cs^+ for the active adsorption site on AMP–PAN. The presence of the anionic surfactants could inhibit the adsorption of Cs^+, but enhance the adsorption of Co^{2+} and Sr^{2+} onto AMP–PAN.

The adsorption of surfactants onto AMP–PAN with and without the metal ions was determined by TOC (total organic carbon) analyzer (Shimadzu Co., Japan). It appears that surfactants were not adsorbing onto the AMP–PAN. Deng et al. [48] performed the batch adsorption equilibrium onto polyacrylonitrile fibers (PANF) to remove Cu. The amount of Cu adsorbed by the PANF was only 1.3 mg/g (= 0.02 mmol/g). This means that the metal did not adsorb onto the surface of the PAN.

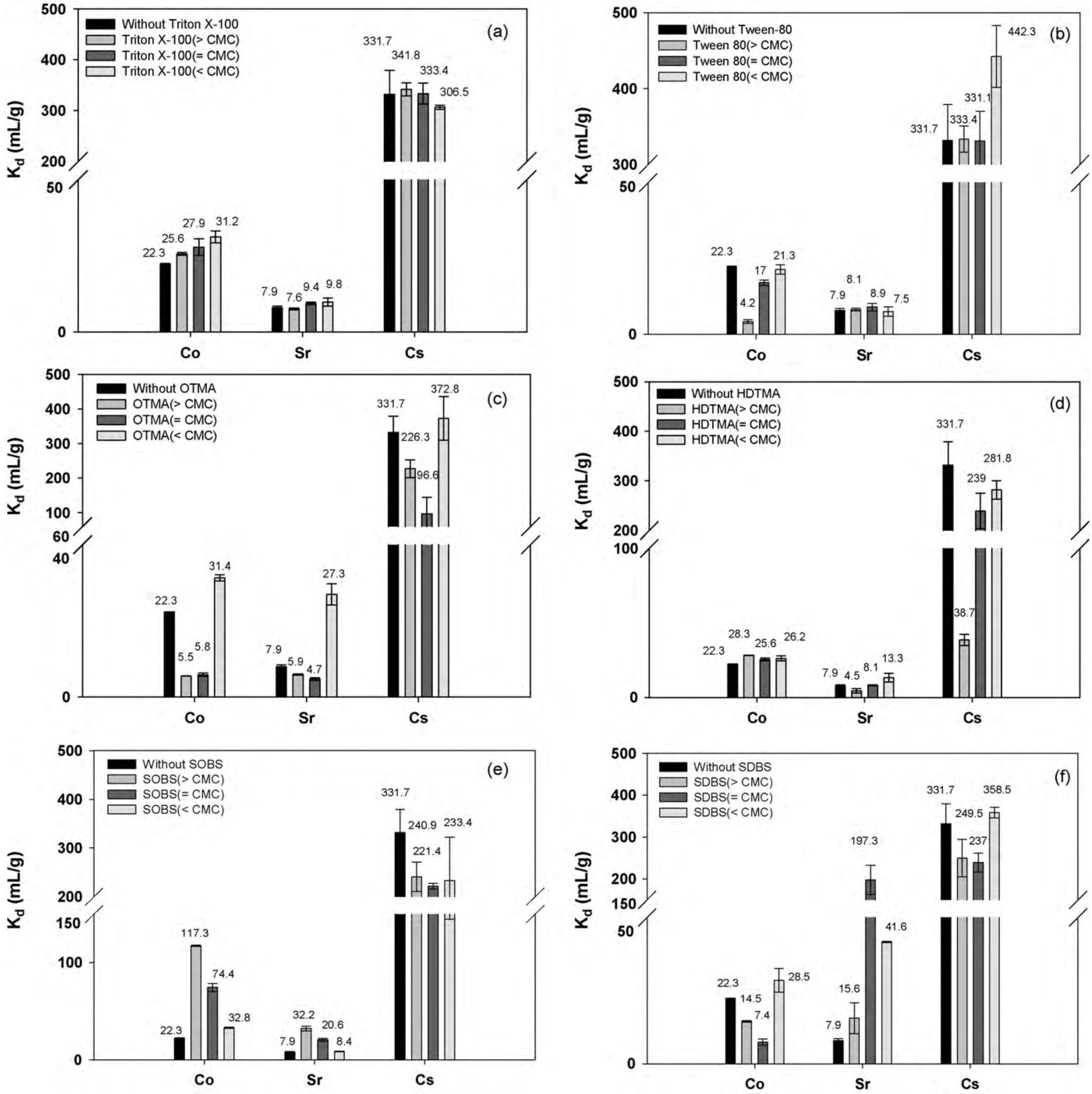

Fig. 8. The effect of surfactants on the distribution coefficient (K_d) values of Co, Sr and Cs (10 mM $Co^{2+}/Sr^{2+}/Cs^{+}$, V/m = 30 mL/g for Co^{2+} and Sr^{2+}, and 75 mL/g for Cs^{+}) for 24 h at 25 °C. (a) Triton X-100, (b) Tween-80, (c) OTMA, (d) HDTMA, (e) SOBS and (f) SDBS.

4. Conclusions

The applicability of AMP–PAN for the removal of Co, Sr and Cs in the radioactive laundry wastewater from nuclear power plants was investigated. The following conclusions are derived from the experimental data:

The adsorption behaviors of the metals onto AMP–PAN were different at different pHs due to variations in metal speciation. The total Co uptake increased at pH above 8 due to precipitation of $Co(OH)_2$. The total Sr uptake also increased with pH followed by sharp increase at pH > 6.5. However, Cs uptake was nearly constant at all pH ranges because Cs exists as Cs^+ at all pH ranges as predicted by MINEQL+.

Adsorption of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–PAN occurs via both physical adsorption due to weak van der Waals forces and the ion exchange mechanism of ammonium molybdophosphate. The result of three adsorption model analyses turned out that AMP–PAN has higher selectivity for Cs^+ than for Co^{2+} and Sr^{2+}.

Na^+ and Ca^{2+} inhibited adsorption of Cs^+ ion onto AMP–PAN by competing on the same sites to exchange the ammonium ions. In the presence of Na^+, the adsorption of Co and Sr were not affected. The presence of Ca^{2+} decreased the adsorption of Co^{2+} onto AMP–PAN because Ca^{2+} has the similar ionic radius compared with Co^{2+}.

Adsorption behaviors of Co^{2+}, Sr^{2+} and Cs^+ onto AMP–PAN in the presence of three different types of surfactants were quiet different.

In the presence of non-ionic surfactants (Trinton X-100 and Tween 80), the adsorptions of all metal cations were hardly affected. However, cationic surfactants (OTMA and HDTMA) affected the adsorption of Co^{2+}, Sr^{2+} and Cs^{+} onto AMP–PAN depending on the type of surfactants. The presence of anionic surfactants (SOBS and SDBS) has highly influenced the adsorption of Co^{2+}, Sr^{2+} and Cs^{+} onto AMP–PAN. This is because the negatively charged anionic surfactant molecules can bind with positively charged metal ions and form metal cation–SDBS or –SOBS complex in the solution.

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References

[1] S. Inan, H. Tel, Y. Altas, Adsorption studies of strontium on hydrous zirconium dioxide, J. Radioanal. Nucl. Chem. 267 (2006) 615–621.

[2] T. Matsuo, T. Nishi, Activated carbon filter treatment of laundry waste water in nuclear power plants and filter recovery by heating in vacuum, Carbon 38 (2000) 709–714.

[3] A.D. Ebner, J.A. Ritter, T.D. Navratil, Adsorption of cesium, strontium and cobalt ions on magnetite and a magnetite-silica composite, Ind. Eng. Chem. Res. 40 (2001) 1615–1623.

[4] A.M. El-Kamash, Evaluation of zeolite a for the sorptive removal of Cs^{+} and Sr^{2+} ions from aqueous using batch and fixed bed column operations, J. Hazard. Mater. 151 (2008) 432–445.

[5] L.D. Danilin, V.S. Drozhzhin, Inorganic sorbents based modified microspheres for the treatment of liquid radioactive waste, Radiochem. 49 (2007) 319–322.

[6] T.A. Todd, V.N. Romanovskiy, A comparison of crystalline silicotitanate and ammonium molybdophosphate-polyacrylonitrile composite sorbent for the separation of cesium from acidic waste, Radiochem. 47 (2005) 398–402.

[7] M.A. Raouf, Potassium hexacyanocobalt ferrate and ammonium molybdophosphate adsorption bags for the removal of ^{137}Cs from aqueous solutions and a simulated waste, J. Chem. Technol. Biotechnol. 79 (2004) 22–29.

[8] H. Mimura, M. Saito, K. Akiba, Y. Onodera, Selective uptake of cesium by ammonium molybdophosphate (AMP)–calcium alginate composites, J. Nucl. Sci. Technol. 38 (2001) 872–878.

[9] F. Sebesta, V. Stefura, Composite ion exchanger with ammonium molybdophosphate and its properties, J. Radioanal. Nucl. Chem. 140 (1990) 15–21.

[10] J.-K. Moon, K.-W. Kim, C.-H. Jung, Y.-G. Shul, E.-H. Lee, Preparation of organic–inorganic composite adsorbent beads for removal of radionuclides and heavy metal ions, J. Radioanal. Nucl. Chem. 246 (2000) 299–307.

[11] T.J. Tranter, R.S. Herbst, T.A. Todd, A.L. Olson, H.B. Eldredge, Evaluation of ammonium molybdophosphate-polyacrylonitrile (AMP–PAN) as a cesium selective sorbent for the removal of ^{137}Cs from acidic nuclear waste solutions, Adv. Environ. Res. 6 (2002) 107–121.

[12] T.A. Todd, N.R. Mann, T.J. Tranter, F. Sebesta, J. John, A. Motl, Cesium adsorption from concentrated acidic tank wastes using ammonium molybdophosphate–polyacrylonitrile composite sorbents, J. Radioanal. Nucl. Chem. 254 (2002) 47–52.

[13] A. Nilchi, H. Atashi, A.H. Javid, R. Seberi, Preparation of PAN-based adsorbers for separation of cesium and cobalt from radioactive wastes, Appl. Radiat. Isot. 65 (2007) 482–487.

[14] J. Smit, R. Van, Ammonium salts of the heteropolyacids as cation exchangers, Nature 181 (1958) 1530–1531.

[15] D. Wolff-Boenisch, S.J. Traina, A comparative study of the effect of desferrioxamine B, oxalic acid, and Na-alginate on the desorption of U(VI) from goethite at pH 6 and 25 °C, Geochim. Cosmochim. Acta 70 (2006) 4356–4366.

[16] A.E. Greenberg, L.S. Clesceri, A.D. Eaton, Standard Method for the Examination of Water and Wastewater, 18th ed., American Public Health Association., Washington, DC, USA, 1992.

[17] C. Caillet, M. Hebrant, C. Tondre, Sodium octyl sulfate/cetyltrimethylammonium bromide catanionic vesicles: aggregate composition and probe encapsulation, Langmuir 16 (2000) 9099–9102.

[18] M.V. Thorsteinsson, J. Richter, L.A. Lee, P. DePhillips, 5-Dodecanoylaminofluorescein as a probe for the determination of critical micelle concentration of detergents using Xuorescence anisotropy, Anal. Biochem. 340 (2005) 220–225.

[19] K. Gogová, B. Maichel, B. Gaš, E. Kenndler, Electrokinetic chromatography with micelles, polymeric and monomeric additives with similar chemical functionality as pseudo-stationary phases, J. Chromatogra. A 916 (207) (2001) 79–87.

[20] S. Suksamranchit, A. Sirivat, Influence of ionic strength on complex formation between poly(ethylene oxide) and cationic surfactant and turbulent wall shear stress in aqueous solution, Chem. Eng. J. 128 (2007) 11–20.

[21] A. Dao, A. Bee, C. Treiner, Adsorption isotherm of sodium octylbenzenesulfonate on iron oxide particles in aqueous solutions, J. Colloid Interface Sci. 204 (1998) 61–65.

[22] E.M.S. Azzam, The synergism effect between sodium dodecylbenzene sulfonate and a block copolymer in aqueous solution, J. Surfactants Deterg. 10 (2007) 13–17.

[23] R. Donat, A. Akdogan, E. Erdem, H. Cetisli, Thermodynamics of Pb^{2+} and Ni^{2+} adsorption onto natural bentonite from aqueous solutions, J. Colloid Interface Sci. 286 (2005) 43–52.

[24] S. Kundu, A.K. Gupta, Arsenic adsorption onto iron oxide-coated cement (IOCC): regression analysis of equilibrium data with several isotherm models and their optimization, Chem. Eng. J. 122 (2006) 93–106.

[25] V.C. Srivastava, I.D. Mall, I.M. Mishra, Equilibrium modelling of single and binary adsorption of cadmium and nickel onto bagasse fly ash, Chem. Eng. J. 117 (2006) 79–91.

[26] L. Boguslavsky, S. Margel, Poly(acrylonitrile) mcirospheres with a narrow size distribution: synthesis by sing-step swelling and properties, Glass Phys. Chem. 31 (2005) 102–114.

[27] M.H. Alizadeh, H. Eshtiagh-Hosseini, M. Mirzaei, A.R. Salimi, H. Razavi, Synthesis, X-ray crystallography characterization, vibrational spectroscopy, and DFT theoretical studies of a new organic-inorganic hybrid material, Struct. Chem. 19 (2008) 155–164.

[28] A. Nilchi, M.R. Hadjmohammadi, S. Garmarodi, R. Saberi, Studies on the adsorption behavior of trace amounts of $^{90}Sr^{2+}$, $^{140}La^{3+}$, $^{60}CO^{2+}$, Ni^{2+} and Zr^{4+} cations on synthesized inorganic ion exchangers, J. Hazard. Mater. 167 (2009) 531–535.

[29] M.K. Harrup, M.G. Jones, L. Polson, B. White, Polymer/silicate composites: new materials for subsurface permeable reactive barriers, J. Sol-Gel Sci. Technol. 47 (2008) 243–251.

[30] G. Crini, H.N. Peindy, F. Gimbert, C. Robert, Removal of C.I. Basic Green 4 (malachite green) from aqueous solutions by adsorption using cyclodextrin-based adsorbent: kinetic and equilibrium studies, Sep. Purif. Technol. 53 (2007) 97–110.

[31] G. McKay, H.S. Blair, J.R. Gardner, Adsorption of dyes on chitin. I. Equilibrium studies, J. Appl. Polym. Sci. 27 (1982) 3040–3057.

[32] P.B. Bhakat, A.K. Gupta, S. Ayoob, S. Kundu, Investigations on arsenic (V) removal by modified calcined bauxite, Colloids Surf. A: Physicochem. Eng. Aspects 281 (2006) 237–245.

[33] H. Buchwald, W.P. Thistlethwaite, Some cation exchange properties of ammonium 12-molybdophosphate, J. Inorg. Nucl. Chem. 5 (1957) 341–343.

[34] C.J. Coetzee, E.F.C.H. Rohwer, Cation exchange studies on ammonium-12-molybdophosphate, J. Inorg. Nucl. Chem. 32 (1970) 1711–1718.

[35] Y.S. Ho, G. McKay, Competitive adsorption of copper and nickel ions from aqueous solution using peat, Adsorption 5 (1999) 409–417.

[36] Z. Aksu, D. Akpınar, Competitive adsorption of phenol and chromium (VI) from binary mixtures onto dried anaerobic activated sludge, Biochem. Eng. J. 7 (2001) 183–193.

[37] J.-S. Chang, C.-C. Chen, Quantitative analysis and equilibrium models of selective adsorption in multimetal systems using a bacterial biosorbent, Sep. Sci. Technol. 33 (1998) 611–632.

[38] R.D. Harter, R. Naidu, An assessment of environmental and solution parameter impact on trace-metal adsorption by soils, Soil Sci. Soc. Am. J. 65 (2001) 597–612.

[39] R. Adhikari, M.V. Singh, Sorption characteristics of lead and cadmium in some soils of India, Geoderma 114 (2003) 81–92.

[40] S. Serrano, F. Garrido, C.G. Campbell, M.T. Garcia, Competitive adsorption of cadmium and lead in acid soils of Central Spain, Geoderma 124 (2005) 91–104.

[41] S. Oh, M.Y. Kwak, W.S. Shin, Competitive sorption of lead and cadmium onto sediments, Chem. Eng. J. 152 (2009) 376–388.

[42] M. Qureshi, K.G. Varshney, Inorganic Ion Exchangers in Chemical Analysis, CRC Press, Boca Raton, FL, 1991, pp. 58.

[43] T.J. Tranter, T.A. Vereshchagina, V. Utgikar, An inorganic microsphere composite for the selective removal of ^{137}Cesium from acidic nuclear waste solutions. 1. Equilibrium capacity and kinetic properties of the sorbent, Solvent Extr. Ion Exch. 27 (2009) 199–218.

[44] E.R. Nightingale, Phenomenological theory of ion solvation. Effective radii of hydrated ions, J. Phys. Chem. 63 (1959) 1381–1387.

[45] C.J. Coetzee, A.J. Vanwyk, Cation exchange studies on ammonium-12-molybdo phosphate-II, J. Inorg. Nucl. Chem. 33 (1971) 1501–1508.

[46] J.-J. Lee, J. Choi, J.-W. Park, Simultaneous sorption of lead and chlorobenzene by organobentonite, Chemosphere 49 (2002) 1309–1315.

[47] Z. Li, R.S. Bowman, Counterion effects on the sorption of cationic surfactant and chromate on natural clinoptilolite, Environ. Sci. Technol. 31 (1997) 2407–2412.

[48] S. Deng, R. Bai, J.P. Chen, Behaviors and mechanisms of copper adsorption on hydrolyzed polyacrylonitrile fibers, J. Colloid Interface Sci. 260 (2003) 265–272.