Sorption of cesium and cobalt ions onto novel zirconium silicophosphate/polyacrylamide nanocomposite

M. R. El-Naggar, I. M. El-Naggar, M. F. El-Shahat and E. S. Abd El-Mohsen

Hot Laboratories Center, Atomic Energy Authority, Cairo, Egypt

Department of Chemistry, Faculty of Science, Ain Shams University, Cairo, Egypt

ABSTRACT

The ion exchange properties of a novel nanocomposite (nano zirconium silicophosphate/polyacrylamide) were tested against Cs⁺ and Co²⁺. Batches were constructed for kinetic and thermodynamic investigations. The highest achievable sorbed amounts of both metal ions were obtained within 120 min. Sorption kinetics of Cs⁺ and Co²⁺ followed the pseudo first- and second-order equations, respectively, and was controlled by the chemical sorption mechanisms. Diffusion of both metal ions into particles of the synthesized nanocomposite was the rate determining step. Both metal ions were weakly bonded to sorbent active sites where low values of activation energy (<42 kJ/mol) were obtained. Linear correlation of the sorption isotherm data to Langmuir and Freundlich equations confirmed the favorability of sorption processes. Raising temperature increased both of the monolayer and relative sorption capacities. The maximum sorbed amounts of Cs⁺ and Co²⁺ were calculated to be 2.06 and 8.75 mmol/g, respectively, with mean free energies reflecting the ion exchange mechanism. All sorption processes were endothermic and were occurred spontaneously where positive ΔHᵣ and negative ΔGᵣ quantities were obtained, respectively, with higher randomness of Cs⁺ than of Co²⁺.

1. Introduction

Treatment is an important step in the radioactive waste management cycle. The radiological analysis of such wastes may be varied according to their origin which either will be nuclear or non-nuclear fuel cycled (IAEA, 2009). Radionuclides of cesium (Cs-134; T₁/₂ = 2.063 y and Cs-137; T₁/₂ = 30.17 y) and cobalt (Co-57; T₁/₂ = 0.745 y, Co-58; T₁/₂ = 0.194 y and Co-60; T₁/₂ = 5.27 y) are presented in the radioactive waste streams as fission and activation products, respectively (Abdelhady, 2013; Abou Elmaaty, 2014). Presence of Cs-137 radionuclide in radioactive waste streams attracted the attention not only due to its relatively high yield per fission of U-235 (6.221% ± 0.069) (Nichols, Aldama, & Verpelli, 2008) but also due to its high solubility and environmental risks (IAEA, 1993). In addition, Co-60 is produced through the activation of corrosion products in the core of the nuclear reactor with considerable amounts. Many effective approaches like ion exchange, chemical precipitation, solvent extraction, and membrane filtration were applied worldwide to treat liquid radioactive wastes (El-Naggar, El-Kamash, El-Dessouky, & Ghonaim, 2008; Mansy, Hassan, Selim, & Kenawy, 2017). The effectiveness which associated with low cost and simplicity of the ion exchange technique made it more favorable than others.

Inorganic-organic nanocompositic ion exchangers are relatively novel designs which recently attract the attention of many authors (Kaur & Jindal, 2018; Pathania, Sharma, Kumar, & Kothiyal, 2014; Pathania, Sharma, & Thakur, 2013). Polyacrylamide (PAA) constitutes a familiar polymer to be used in the synthesis of such composites among the other organic. Based on the co-part with PAA, the produced nanocomposites may have catalytic (Abou El Fadl, 2016; Mahdavi & Rahmani, 2016), antibacterial (Hussain & Jaisankar, 2017; Li et al., 2013; Mahdavi, Rahmani, & Shahverdi, 2017), biointeractional (Fonseca, 2018) and enhanced oil recovery (Singh & Mahto, 2017) applications. Additionally, the majority of authors utilized the PAA-based nanocomposites in adsorption applications like water purification (Atta, Al-Lohedan, Ezzat, Issa, & Oumi, 2016; Manafi et al., 2017) as well as removal of dyes (Hadizade, Binaeian, & Emami, 2017; Zhou, Wu, Lei, & Negulescu, 2014), Hg (II) (Hosseinzadeh & Ramin, 2016; Saad et al., 2016), lead (II) (Güçlü et al., 2010; Xu et al., 2014), Fe (III) (Natkański, Kustrowski, Białas, Piwowarska, & Michalik, 2013), Cu (II) (Güçlü et al., 2010), and moisture (Mirbagheri & Hill, 2017). Also, application of such nanocompositic hydrogels in the nuclear sector to remove U(VI) from aqueous solutions was carried out (Ortabor et al., 2013). Literature survey about zirconium phosphate (ZrP) nanoparticles revealed that there are limited efforts to incorporate their forms into an organic polymer. Recently, Pathania and coworker succeeded to fabricate different designs of ZrP-based nanocomposites. They prepared a polyaniline-based zirconium (IV) silicophosphate (ZrSiP) nanocomposite for photocatalytic and antimicrobial activities (Pathania et al., 2014) as well as for...
remediation of methylene blue dye from wastewater (Gupta, Pathania, Kothiyal, & Sharma, 2014). They also prepared a pectin-based ZrSiP nanocomposite for heavy metal separation and antimicrobial activities (Pathania et al., 2015).

These efforts and others reflected a gap in the synthesis and applications of PAA-based ZrSiP nanocomposite. Thus, the present study aimed to assess the ion-exchange property of ZrSiP/PAA nanocomposite, which was presynthesized in our previous work (Abd El-Mohsen, El-Naggar, El-Naggar, & El-Shahat, 2014), and to exploit it in sorption of cesium and cobalt ions from their aqueous solutions. In this respect, factors affecting the sorption processes such as contact time, pH or temperature were investigated. Kinetic and equilibrium sorption data were analyzed using three different mathematical models for each. Thermodynamic parameters were also calculated in order to gain more insights about the sorption processes.

2. Materials and methods

2.1. Chemicals and reagents

Sodium metasilicate, cetyl trimethyl ammonium bromide (CTAB), sodium lauryl sulfate (SLS) and zirconium oxychloride are products of Sigma Aldrich and were used as silicon, charged cation surfactant, charged anion surfactant and zirconium ion sources, respectively. While acrylamide, diammonium hydrogen phosphate, cesium chloride, cobalt chloride, and potassium per sulfate were products of BDH. Glycerol was product of WinLab Co.

2.2. Synthesis and characterization of ZrSiP/PAA nanocomposite

Synthesis of ZrSiP/PAA nanocomposite was carried out by a simple intercalation method as described in our previous work (Abd El-Mohsen et al., 2014).

Sodium metasilicate (0.1 M) and diammonium hydrogen phosphate (0.1 M) were prepared and mixed in 1:1 volumetric ratio. CTAB and SLS were added (~5 g of both), at vigorous stirring conditions. Then, zirconium oxychloride (0.1 M) was added, at a rate of 3 ml/min. The obtained mixture was kept in vigorous stirring conditions for 12 h to attain complete reaction. The resultant suspension was highly centrifuged to obtain ZrSiP nanoparticles which then were filtrated, washed several times using bi-distilled water and calcined at 400°C to remove templates. The intercalation of the prepared ZrSiP nanoparticles into PAA matrix was carried out. 50 g acrylamide was dissolved in 500 ml bi-distilled water. Then, 500 ml of 0.1 M potassium persulfate solution was added drop wise, with stirring. Finally, ZrSiP nanoparticles were added at 25% loading with 4 h stirring until complete polymerization (Figure 1). The obtained product was gelatinous pale yellow in color. This product was dried at 50°C, crushed and heated in glycerol (~290°C) to reach the T_g value of PAA at which ZrSiP/PAA nanocomposite has a spherical shape. Then, sieving was carried out to obtain nanocomposite particles of ~38 µm diameter.

2.3. Effect of cation hydrolysis

The hydrolysis of CsCl and CoCl_2 salts in an aqueous solution was studied with the visual MINTEQA2 (MinteqA2, 2006) at constant initial ionic concentration, ionic strength, temperature and different pH values.

2.4. Sorption studies

Kinetic and equilibrium batch experiments were investigated to study the sorption of Cs^+ and Co^{2+} from aqueous solutions. Nanocomposite material (0.02 g) was put into 25.0 mL colorimetric tube containing 10 mL of a metal ion solution. Triplet mixtures were shaken

Figure 1. Schematic diagram of zirconium silicophosphate/polyacrylamide nanocomposite (Abd El-Mohsen et al., 2014).
vigorously at 298, 313 or 333 K. Solids was separated from liquids by centrifugation at 5500 rpm. Filtrates were analyzed using atomic absorption spectrophotometer (Buck Scientific, VGP 210 using air acetylene flame, Kyoto-Japan) to determine the concentrations of Cs$^+$ and Co$^{2+}$ at the end of each batch test.

2.4.1. Kinetic investigations
The effect of contact time on the removal ($R$, %) and the sorbed amounts at different time intervals ($Q_t$, mmol/g) were calculated as follows:

$$\% R = \frac{C_0 - C_t}{C_0} \times 100 \quad (1)$$

where $C_0$ and $C_t$ are the metal ion concentrations at the beginning and after time $t$, respectively.

$$Q_t = \frac{(C_0 - C_t) V}{m} \quad (2)$$

where $V$ and $m$ are volume of the liquid phase (L) and mass of the solid phase (g), respectively. Different kinetic models were applied to investigate rate determining steps for the sorption processes.

2.4.2. Equilibrium investigations
Isotherms for the sorption of Cs$^+$ and Co$^{2+}$ onto ZrSiP/PAA nanocomposite were constructed. Experiments were done at concentration range from $10^{-3}$ to $10^{-2}$ mmol and different temperatures (298, 313 or 333 K). The amount of sorbed metal ion per unit weight of sorbent at equilibrium ($Q_e$, mmol/g) was calculated according to:

$$Q_e = \frac{(C_0 - C_e) V}{m} \quad (3)$$

where $C_0$ and $C_e$ are the metal ion concentrations at the beginning and at equilibrium, respectively.

3. Results and discussion
3.1. Synthesis and characterization of ZrSiP/PAA nanocomposite
Spherical ZrSiP/PAA nanocomposite particles were synthesized, in their hydrogen form, and characterized as mentioned in our previous work (Abd El-Mohsen et al., 2014) (Figure 1). The obtained pale yellow nanocomposite spheres were subjected to the FT-IR analysis in order to confirm the intercalation of ZrSiP nanoparticles into completely polymerized acrylamide monomers (Figure 2). Assignments of the solely ZrSiP nanoparticles and their corresponding nanocomposite are summarized in Table 1. Absence of the stretching vibrations of C = C bonding confirmed the complete polymerization of acrylamide monomers (Maclachian & Morgan, 1992). Hydrogen bonding between ZrSiP nanoparticles and PAA matrix has been proofed through the vibration band at 1212 cm$^{-1}$ which related to the delocalized electrons on the carbonyl group as a result of the hydrogen bonding (Pimentel & McClellan, 1960). Particles of the synthesized ZrSiP were in the nanoscale (45 nm) as evidenced by the TEM examinations (Figure 3).

3.2. Speciation analysis
Hydrolysis of cesium and cobalt metal ions inside the aqueous chloride solutions (Figure 4) was studied at $10^{-4}$ M initial ion concentration, ionic strength of 0.1, temperature of 298 K and different pH values of the solution ranging from 1 to 13. pH has a significant impact on the species of cobalt where up to pH of 8.0 Co$^{2+}$ was the predominant phase. After such pH value, other species of cobalt began to appear gradually at the expense of Co$^{2+}$. Thus, all sorption experiments of Cs$^+$ and Co$^{2+}$ onto the synthesized nanocomposite were performed at...

---

**Figure 2.** FT-IR spectra of ZrSiP nanoparticles and ZrSiP/PAA nanocomposite (Abd El-Mohsen et al., 2014).
Table 1. FT-IR assignments of solely zirconium silicophosphate nanoparticles and after intercalation into polyacrylamide matrix.

| cm⁻¹ | Assignment                  | cm⁻¹ | Assignment                  |
|------|-----------------------------|------|-----------------------------|
| 3443 | Hydroxyl groups             | 3430 | Hydroxyl groups             |
| 1635 | P – O; symmetric str.       | 3202 | NH₂; symmetric str.         |
| 1036 | Si – O; asymmetric str.     | 3926 | CH₂; symmetric str.         |
| 524  | Zr – O; asymmetric str.     | 2858 | CH; symmetric str.          |
| 423  | Si – OH; bending            | 1663 | Carbonyl group              |
|      |                             | 1446 | CH; symmetric str.          |
|      |                             | 1212 | C – O; str.                 |
|      |                             | 1107 | Si – O; asymmetric str.     |
|      |                             | 614  | Zr – O; asymmetric str.     |

str. = stretching

pH range from 7.5 to 8.0 to attain the highest percentage of free cations.

3.3. Sorption kinetic studies

3.3.1. Effect of contact time

The effect of contact time on the removal percentage (Figure 5) and the sorbed amounts in mmol/g (Figure 6) of Cs⁺ and Co²⁺ from their aqueous solutions was studied at different temperatures where the initial concentration was constant. The sorbed amounts and the associated removal of Co²⁺ were greater than those of Cs⁺ with a positive effect of temperature reflecting the endothermic natures of sorption. The highest achievable sorbed amounts of both metal ions were obtained within the first 2 h of contact time where no considerable sorbed amounts were observed after this period (Figure 6). During the first half hour of contacting at 298 K, about 65.90% and 70.98% of the sorbed amounts were reached for Cs⁺ and Co²⁺, respectively. This may be due to the higher availability of both metal ions around the environment of ZrSiP/PAA nanocomposite at these early ages of contact time. After an additional half-hour of contacting, these percentages were increased to values of 81.82 and 85.80, respectively. Sorption of both metal ions almost becomes constant with increase in contact time. Therefore, the contact time of 120 min was considered as optimum sorption duration for both metal ions.

3.3.2. Kinetic modeling

The experimentally obtained sorption data were analyzed using three kinetic models in order to explore

Figure 3. TEM of zirconium silicophosphate nanoparticles (a) and after intercalation into polyacrylamide matrix (b) (Abd El-Mohsen et al., 2014).

Figure 4. Concentration percentages of Cs⁺ and Co²⁺ as a function of pH for 0.1 ionic strength and 298 K.
the mechanisms by which Cs$^{+}$ and Co$^{2+}$ were sorbed onto the synthesized ZrSiP/PAA nanocomposite.

3.3.2.1. Pseudo first-order kinetic model. This model of Lagergren was the first equation for the sorption in solid/liquid systems (Lagergren, 1898). The basic assumption of this model is that each surface sorption site can sorb one metal cation. The general expression of this model is as follows:

$$\log (Q_e - Q_t) = \log Q_e - \frac{k_1}{2.303}t$$

where $k_1$ is the pseudo first-order rate constant (min$^{-1}$). Both $k_1$ and $Q_e$ can be calculated from the slope and intercept, respectively, of the linear fitting after plotting log ($Q_e - Q_t$) versus $t$. Lagergren’s model rendered the rate of Cs$^{+}$ and Co$^{2+}$ to occupy the active sites of the studied nanocomposite. Figure 7 represents the linear fitting of log ($Q_e - Q_t$) vs. contact time ($t$) plots, at different temperatures. Values of $Q_e$ (mmol/g) and $k_1$ (min$^{-1}$) were calculated from intercepts and slopes of such plots, respectively (Table 2). The obtained correlation coefficients ($R^2$) of Cs$^{+}$ (0.996–0.998) were better than those of Co$^{2+}$ (0.986–0.999) indicating the applicability of the pseudo first-order equation to describe sorption of the former. But the calculated $Q_e$ values were still away from the experimental ones for both metal ions. Thus, other models were applied to describe the sorption kinetics onto the synthesized nanocomposite.

3.3.2.2. Pseudo second-order kinetic model. The basic assumption of this model was that one sorbate was sorbed onto two surface sites (Ho & McKay, 1999). The pseudo second-order equation is expressed as:

$$\frac{t}{Q_t} = \frac{1}{k_2Q_e} + \frac{1}{Q_e}t$$

Figure 5. Effect of contact time on the uptake (%) of a) Cs$^{+}$ and b) Co$^{2+}$ sorbed onto ZrSiP/PAA nanocomposite, at different temperature values.

Figure 6. Effect of contact time on the sorbed amounts (mmol/g) of a) Cs$^{+}$ and b) Co$^{2+}$ sorbed onto ZrSiP/PAA nanocomposite, at different temperature values.
where \( k_2 \) is the rate constant of the pseudo second-order equation (g/mmol min). If the initial sorption rate \( h \) (mmol/g min) is:

\[
h = k_2 Q^2
\]  

(6)

Then, Equation (6) becomes:

\[
\frac{t}{Q_t} = \frac{1}{h} + \frac{1}{Q_s} t
\]  

(7)

If the pseudo second-order kinetic model is applicable the plot of \( t/Q_t \) against \( t \) should give a linear relationship, from which \( Q_s, k_2 \) and \( h \) can be determined from the slope and intercept. The kinetic plots of \( t/Q \) vs. contact time \( t \) for sorption of Cs\(^+\) and Co\(^{2+}\) onto ZrSIP/PAA nanocomposite were depicted in Figure 8. Initial sorption rates \( h \) (mmol/g min) and sorbed amounts \( Q_s \) (mmol/g) as well as rate constants \( k_2 \) (g/mmol min) were also calculated from slopes and intercepts, respectively (Table 2). The correlation coefficients \( (R^2) \), unlike Lagergren equation, indicated the better fit of pseudo second-order model to sorption of Co\(^{2+}\) (0.990–0.992) than Cs\(^+\) (0.982–0.984). Also, all calculated \( Q_s \) values were close to the experimentally obtained ones, for both metal ions. These assumed that all sorption processes were controlled by the chemical sorption mechanism in which valance forces through sharing or exchanging of electrons between sorbent and sorbate were involved (Costodes, Fauduet, Porte, & Dela-Croix, 2003; El-Naggar, Aglan, & Sayed, 2013).

### 3.3.2.3. Homogeneous particle diffusion model (HPDM)

In this model, the rate-determining step of sorption is normally described by either the diffusion of ions through the liquid film surrounding the particle, called film diffusion, or the diffusion of ions into the sorbent beads, called particle diffusion mechanism. Nernst-Plank equation (Helfferich, 1962), which takes into account both concentration and electrical gradients of exchanging ions into the efflux equation, was used to establish HPDM equations. In case of the particle, diffusion controls the process, the following relation can be utilized to calculate the diffusion coefficient:

\[
F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -\frac{D_n t n^2}{r_o^2} \right)
\]  

(8)

\[
F(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left( -n^2 B t \right)
\]  

(9)

\[
B = \frac{n^2 D_i}{r_o^2}
\]  

(10)

where \( F \) is the fractional attainment of equilibrium at time \( t \) \( (F = Q_t/Q_s) \), \( B \) is the time constant, \( D_i \) is the effective diffusion coefficient of metal ion, \( r_o \) is the...
radius of the nanocomposite sorbent particle (38 µm, assuming the particles are spheres), and \( n \) are integers 
1, 2, 3, . . .

Equation (10) was rearranged and the natural logarithm was taken to obtain the following equation:

\[
Bt = -0.4977 - \ln(1 - F) \tag{11}
\]

If the plots are straight lines passing through the origin, the sorption rates are governed by particle diffusion mechanism; otherwise, it is governed by film diffusion (Helfferich, 1962). This model was applied to distinguish between the film and particle diffusion mechanisms of the studied metal ions through the \( Bt \) vs. time plots (Figure 9). \( Bt \) values were calculated regarding \( F \) values according to Equation (11), under the effect of temperature. Linear plots, passing through the origin, were obtained indicating that the sorption processes were particle diffusion-controlled, for both metal ions. Hence, values of the effective diffusion coefficient (\( D_e \), m\(^2\)/s) are calculated using the slopes of such straight lines and are given in Table 3. Walker and Weatherly stated that orders of \( D_e \) values could distinguish between the physical and chemical sorption mechanisms where the former records orders from \( 10^{-9} \) to \( 10^{-6} \) m\(^2\)/s while the later records orders from \( 10^{-17} \) to \( 10^{-9} \) m\(^2\)/s (Walker & Weatherly, 1999). Data in Table 3 strengthened those obtained by the pseudo second-order model in which chemical sorption is the controlling mechanism where \( D_e \) values recorded orders of \( 10^{-17} \) cm/s.

Figure 10 represents the plots of \( \ln D_e \) vs. time which were depicted in order to examine the validation of Arrhenius equation’s linear form:

\[
\ln D_e = \ln D_o - \left( \frac{E_a}{RT} \right) \tag{12}
\]

where \( D_o \) (m\(^2\)/s) and \( E_a \) (kJ/mol) are the pre-exponential constant and the energy of activation which can be calculated from intercepts and slopes, respectively. The obtained straight lines in Figure 10, with considerable \( R^2 \) values, confirmed the validity of Arrhenius equation.

Figure 9. \( Bt \) versus time plots for sorption of a) Cs\(^+\) and b) Co\(^{2+}\) onto ZrSiP/PAA nanocomposite, at different temperature values.
Values \( E_a \) and entropy of activation \( (\Delta S^\ddagger, \text{J/mol K}) \) were calculated and were given in Table 3. The obtained low values of \( E_a \) (< 42 kJ/mol), for both metal ions, reflected the weak interaction between ZrSiP/PAA nanocomposite and Cs\(^+\) or Co\(^{2+}\) during the chemical sorption mechanisms of them (Scheckel & Sparks, 2001).

### 3.4. Equilibrium investigations

Beside the sorption kinetics, equilibrium investigations are commonly performed to understand the sorption mechanisms. These investigations are usually expressed by an isotherm equation in which a relation between the mass of sorbate per unit weight of sorbent \( (Q_e, \text{mmol/g}) \) and the liquid phase sorbate \( (C_e, \text{mmol/L}) \) at constant pH and concentration (Zhou et al., 2014). Hence, sorption isotherms of Cs\(^+\) and Co\(^{2+}\) onto ZrSiP/PAA nanocomposite were constructed and shown in Figure 11. All isotherms were regular and positive with liquid phase concentration for both metal ions. Langmuir, Freundlich and D-R are conventional isotherm models and were applied to determine isotherm’s parameters.

#### 3.4.1. Langmuir isotherm model

Langmuir isotherm is one of the most widely used models to study the adsorption processes in solid-liquid systems. This model describes the monolayer homogeneous distribution of adsorbate molecules onto identical active sites of adsorbent. Such model was expressed using (Langmuir, 1918):

\[
Q_e = \frac{Q^o b C_e}{1 + b C_e} \tag{13}
\]

where \( C_e \) is the equilibrium concentration of the sorbed ion (mmol/L), \( Q^o \) is the monolayer adsorption capacity (mmol/g) and \( b \) is the constant related to the free energy of adsorption \( (b \propto e^{-\Delta G/RT}) \). Values of \( b \) and \( Q^o \) can be determined graphically by linearizing and rearrangement of Equation 12:

\[
\frac{C_e}{Q_e} = \frac{1}{Q^o b} + \frac{1}{Q^o} C_e \tag{14}
\]

By plotting \( C_e \) versus \( C_e/Q_e \), the slope equals \( 1/Q^o \) while the intercept equals \( 1/Q^o b \). The constant ‘\( b \)’ can be determined from slope and intercept, representing the affinity between the adsorbent and sorbate (El-Naggar & Amin, 2018).

The linear form of Langmuir isotherm model (Equation 14) was graphically presented in Figure 12 by plotting \( C_e/Q_e \) vs. \( C_e \) values. Langmuir isotherm parameters were calculated from slopes and intercepts of the fitted experimental data and were given in Table 4. It is clear that the monolayer sorption capacities were increased by increasing temperature for both of Cs\(^+\) (1.17–1.37 mmol/g) and Co\(^{2+}\) (3.16–3.21 mmol/g) with a Co\(^{2+}\) priority of more than twice of Cs\(^+\), at any temperature value. This temperature effect may be due to possible available active sites which were not easily accessible at lower temperatures. The essential Langmuir equilibrium parameters
El-Naggar & Amin, 2018, were also calculated using:

$$R_L = \frac{1}{1 + bC_o}$$  \hspace{1cm} (15)$$

where $C_o$ is the highest original concentration of either Cs$^+$ or Co$^{2+}$ (mmol/L). The essentiality of such parameter comes from its ability to describe the type of isotherm which may be irreversible ($R_L = 0$), favorable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavorable ($R_L > 1$). Data in Table 4 indicated the favorability of the constructed isotherms for both metal ions.

### 3.4.2. Freundlich isotherm model

The Freundlich isotherm is an empirical model which can be used to describe the sorption processes. It involves heterogeneous adsorption surface and active

#### Table 4. Langmuir and Freundlich isotherm parameters of Cs$^+$ and Co$^{2+}$ sorbed onto ZrSiP/PAA nanocomposite, at different temperatures.

| Metal ion | Temperature, K | $Q^o$, mmol g$^{-1}$ | $b$, L mmol$^{-1}$ | $R^2$ | $R_L$ | $n$ | $K_f$, mmol g$^{-1}$ | $R^2$ |
|-----------|----------------|----------------------|-------------------|-------|-------|-----|---------------------|-------|
| Cs$^+$    | 298            | 1.17                 | 2.73              | 0.998 | 3.53 E-2 | 4.29 | 0.76                | 0.947 |
|           | 313            | 1.28                 | 3.73              | 0.999 | 2.61 E-2 | 4.56 | 0.89                | 0.901 |
|           | 333            | 1.37                 | 4.33              | 0.999 | 2.26 E-2 | 4.62 | 0.94                | 0.933 |
| Co$^{2+}$ | 298            | 3.16                 | 0.92              | 0.996 | 9.80 E-2 | 1.91 | 1.32                | 0.962 |
|           | 313            | 3.19                 | 0.96              | 0.996 | 9.43 E-2 | 1.92 | 1.36                | 0.959 |
|           | 333            | 3.21                 | 1.03              | 0.996 | 8.85 E-2 | 1.93 | 1.41                | 0.952 |
sites with different energies. The mathematical expression of this model is shown in Equation 16 (Freundlich, 1906):

\[ Q_e = K_F C_e^{1/n} \]  

(16)

where \( K_F \) is a constant indicative of the relative sorption capacity (mmol/g) and \( 1/n \) is a constant indicative of the intensity of the sorption process. The logarithmic form of the above equation gives a linear relationship as shown below:

\[ \log Q_e = \log K_F + \frac{1}{n} \log C_e \]  

(17)

This model assumes the multilayer sorption onto heterogeneous surfaces. Its linear form was given in Equation 17 and was presented in Figure 13 by plotting \( \log Q_e \) vs. \( \log C_e \) values. The constants of Freundlich model (\( K_F \) and \( 1/n \)) were calculated from slopes and intercepts using linear fitting method and were given in Table 4. The values of \( n \) indicate the effectiveness of an isotherm to be favorable \((0 < 1/n< 1)\), unfavorable \((1/n > 1)\) or irreversible \((1/n = 0)\). The relative sorption capacity (\( K_F \), mmol/g) was increased by increasing temperature, for both metal ions with a tendency of the synthesized nanocomposite toward \( \text{Co}^{2+} \). It was observed that all \( 1/n \) values lied in the range of \( 0 < 1/n < 1 \) indicating that all sorption processes were favorable, especially in high concentration region. This may be due to the adsorbate pressure (McKay, El Geundi, & Nassar, 1997) which creates new active sites that are not accessible at low concentrations.

### 3.4.3. Dubinin–Radushkvich (D–R) isotherm model

In order to study the nature of the sorption processes, the D–R isotherm was also verified in the form (Dubinin & Radushkevich, 1947):

\[ \ln q_e = \ln q_m - \beta \varepsilon^2 \]  

(18)

where \( q_m \) is the maximum amount of ion that can be sorbed onto unit weight, i.e. sorption capacity (mmol/g), \( \beta \) is a constant related to the sorption energy \((\text{mol}^2/\text{kJ}^2)\) and \( \varepsilon \) is the Polanyi potential \(=RT\ln(1 + 1/C_e)\), where \( R \) is the gas constant (kJ/mol K), and \( T \) is the absolute temperature (K). The mean free energy of sorption is the free energy change when one mole of ion is transferred to the surface of the nanocomposite from infinity in the solution, and it is calculated from:

\[ E = (–\beta)^{-1/2} \]  

(19)

The magnitude of mean free energy, \( E \), can be related to the reaction mechanism. If \( E \) is in the range of 8–16 kJ/mol, sorption is governed by ion exchange (Helfferich, 1962). In the case of \( E < 8.0 \) kJ/mol, physical forces may affect the sorption mechanism.

This model is more general than Langmuir and Freundlich models where it is based on Polanyi’s potential theory rejecting the homogeneous surfaces as well as active sites of equal energies. The experimentally obtained sorption data were linearly correlated to D–R isotherm (Figure 14). The calculated isotherm parameters and \( R^2 \) were given in Table 5. The synthesized nanocomposite recorded higher \( R^2 \) values and also higher sorption capacity range toward \( \text{Co}^{2+} \) (8.41–8.75 mmol/g) than \( \text{Cs}^+ \) (1.78–2.06 mmol/g). These sorbed amounts, for both metal ions, were ion-exchange controlled where their mean free energies \((E, \text{kJ/mol})\) values were ranged between 8 and 16 kJ/mol (Helfferich, 1962).

### 3.5. Thermodynamic parameters

The thermodynamic parameters for the presented sorption processes of \( \text{Cs}^+ \) and \( \text{Co}^{2+} \) onto synthesized ZrSiP/PAA nanocomposite were calculated. The thermodynamic equilibrium constant \( K_c \) was calculated as a product of Langmuir isotherm model parameters \((Q \times b)\) (El-Kamash, 2008). Excess Gibbs free energy of sorption process was calculated according to:

\[ \Delta G^0 = -RT \ln K_c \]  

(20)

Figure 13. Plots of Freundlich isotherm model for the sorption of a) \( \text{Cs}^+ \) and b) \( \text{Co}^{2+} \) onto ZrSiP/PAA nanocomposite, at different temperatures.
where $K_c$ is the thermodynamic equilibrium constant, $R$ is the gas constant and $T$ is the absolute temperature (K). The spontaneity of a sorption process can be identified by the aid of its free energy, $\Delta G^\circ$. The reaction occurs spontaneous when $\Delta G^\circ$ recorded negative quantity. The entropy change ($\Delta S^\circ$) and the enthalpy change ($\Delta H^\circ$) were also estimated according to:

$$\ln K_c = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad (21)$$

$\Delta H^\circ$ and $\Delta S^\circ$ values were calculated from slopes and intercepts of linear fitting data of Figure 15, respectively. All thermodynamic parameters are given in Table 6. Data revealed that all sorption processes were endothermic and occurred spontaneously where positive $\Delta H^\circ$ and negative $\Delta G^\circ$ quantities were obtained, respectively. Also, data confirmed the strengthening of adsorbate-adsorbent interactions at higher temperatures where positive relations were observed between $K_c$ values and temperature, for both studied metal ions. The higher positive values of $\Delta S^\circ$ of Cs$^+$ than Co$^{2+}$ inferred the higher randomness of the former during the redistribution of its energy over the surface of ZrSiP/PAA nanocomposite (Chen, Li, Zhao, Tan, & Wang, 2007).

### 4. Conclusions

The present work studied the sorption characteristics of pre-synthesized novel zirconium silicophosphate polyacrylamide nanocomposite ion exchanger in its hydrogen...
form. Batch sorption experiments of Cs\(^+\) and Co\(^{2+}\) from their aqueous solutions were carried out. Factors like pH, temperature, contact time and initial ion concentration, which are commonly affect on sorption processes, were examined. The highest achievable sorbed amounts of both metal ions were obtained within the first 2 h of contact time where no considerable sorbed amounts were observed after this period. The pseudo first-order model was more applicable in description of sorption of Cs\(^+\) onto ZrSiP/PAA nanocomposite than Co\(^{2+}\). The sorption processes were particle diffusion-controlled, for both metal ions. Values of activation energy and entropy of activation were calculated. The obtained low values of activation energy (<42 kJ/mol), for both metal ions, reflected the weak interaction between ZrSiP/PAA nanocomposite and Cs\(^+\) or Co\(^{2+}\) during the chemical sorption mechanisms of them. The monolayer sorption capacities were evaluated using Langmuir isotherm model and were found to be increased by increasing temperature for both Cs\(^+\) (1.17–1.37 mmol/g) and Co\(^{2+}\) (3.16–3.21 mmol/g). The essential Langmuir equilibrium parameters, \(R_e\), were also calculated indicating the favorability of the constructed isotherms for both metal ions. The relative sorption capacities were calculated using Freundlich isotherm model and were found to be increased by increasing temperature, for both metal ions with a tendency of the synthesized nanocomposite toward Co\(^{2+}\). The synthesized nanocomposite recorded higher \(R^2\) values and also higher sorption capacity toward Co\(^{2+}\) (8.41–8.75 mmol/g) than Cs\(^+\) (1.78–2.06 mmol/g). The ion exchange mechanisms were observed to control all sorption processes. Data revealed that all sorption processes were endothermic and were occurred spontaneously where positive \(\Delta H^o\) and negative \(\Delta G^o\) quantities were obtained, respectively. The higher positive values of \(\Delta S^o\) of Cs\(^+\) than Co\(^{2+}\) inferred the higher randomness of the former during the redistribution of its energy over the surface of ZrSiP/PAA nanocomposite. According to the experimentally obtained data, it is recommended to apply nanocomposite materials like that assessed in the present study in the treatment/purification of radioactive waste streams.

**Discourse statement**

No potential conflict of interest was reported by the authors.

**References**

Abd El-Mohsen, E. S., El-Naggar, M. R., El-Naggar, I. M., & El-Shahat, M. F. (2014). Evaluation of zirconium silicophosphate material for the removal of copper ions from waste water. *Journal of Nuclear Technology and Applied Sciences*, (23), 319–330.

Abdelhady, A. (2013). Radiological performance of hot water layer system in open pool type reactor. *Alexandria Engineering Journal*, 52, 159–162.

Abou El Fadl, F. I. (2016). Synthesis and characterization of chitosan-poly(acrylamide-co-acrylic acid) magnetic nanocomposite hydrogels for use in catalysis. *Russian Journal of Applied Chemistry*, 89(10), 1673–1680.

Abou Elmatta, T. (2014). Experimental investigation of the hot water layer effect on upward flow open pool reactor operability. *Arab Journal of Nuclear Sciences and Applications*, 47(3), 7–125.

Atta, A. M., Al-Lohedan, H. A., Ezzat, A. O., Issa, Z. A., & Oumi, A. B. (2016). Synthesis and application of magnetite polyacrylamide amino-amidoxime nano-composites as adsorbents for water pollutants. *Journal of Polymer Research*, 23, 69–79.

Chen, C., Li, X., Zhao, D., Tan, X., & Wang, X. (2007). Adsorption kinetic, thermodynamic and desorption studies of Th(IV) on oxidized multi-wall carbon nanotubes. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 302, 449–454.

Costodes, V. C., Fauduet, H., Porte, C., & Dela-Croix, A. (2003). Removal of Cd(ll) and Pb(II) ions, from aqueous solutions, by adsorption on sawdust of Pinus sylvestris. *Journal of Hazardous Materials*, 105, 121–142.

Dubiniv, M. M., & Radushkevich, L. V. (1947). Equation of the characteristic curve of activated charcoal. *Proceedings of the Academy of Sciences, Physical Chemistry Section*, 55, 331.

El-Kamash, A. M. (2008). Evaluation of zeolite A for the sorptive removal of Cs\(^+\) and Sr\(^{2+}\) ions from aqueous solutions by batch and fixed bed column operations. *Journal of Hazardous Materials*, 151, 432–445.

El-Naggar, M. R., Aglan, R. F., & Sayed, M. S. (2013). Direct incorporation method for the synthesis of molybdophosphate/MCM-41 silica composite: Adsorption study of heavy metals from aqueous solutions. *Journal of Environmental Chemical Engineering*, 1, 516–525.

El-Naggar, M. R., & Amin, M. (2018). Impact of alkali cations on properties of metakaolin and metakaolin/slag geopolymers: Microstructures in relation to sorption of \(^{134}\)Cs radionuclide. *Journal of Hazardous Materials*, 344, 913–924.

El-Naggar, M. R., El-Kamash, A. M., El-Dessouky, M. I., & Ghonaïm, A. K. (2008). Two-step method for preparation of NaA-X zeolite blend from fly ash for removal of cesium ions. *Journal of Hazardous Materials*, 154, 963–972.

Fonseca, L. C., de Araújo, M. M., de Moraes, A. C. M., Da Silva, D. S., Ferreira, A. G., Franqui, L. S., … Alves, O. L. (2018). Nanocomposites based on graphene oxide and mesoporous silica nanoparticles: Preparation, characterization and

| Metal ion | Temperature, K | \(K_f\) | \(\Delta G^o\), kJ mol\(^{-1}\) | \(\Delta H^o\), kJ mol\(^{-1}\) | \(\Delta S^o\), J mol\(^{-1}\)K\(^{-1}\) |
|-----------|----------------|-----|-----------------|-----------------|-----------------|
| Cs\(^+\)   | 298            | 3.19| 2.87            | 14.23           | 57.76           |
|           | 313            | 4.77| 4.07            | 16.24           | 57.76           |
|           | 333            | 5.93| 4.93            | 16.24           | 57.76           |
| Co\(^{2+}\)| 298            | 2.91| 2.65            | 3.01            | 18.98           |
|           | 313            | 3.06| 2.91            | 3.01            | 18.98           |
|           | 333            | 3.31| 3.31            | 3.31            | 18.98           |
