Utilization of synthetic nano-cryptomelane for enhanced scavenging of cesium and cobalt ions from single and binary solutions

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Abstract
The feasibility of using nano-cryptomelane for elimination of cobalt and cesium metal ions from their single and binary solutions was studied. In this respect, the material was prepared and characterized to confirm its chemical composition and structure. Results illustrate that the synthesized nano-cryptomelane has a tunnel structure with particle size ranged between 4 and 6 nm. The material feasibility was detected by conducting a series of batch experiments for determination of the kinetic and equilibrium performance of the removal process. All characteristic Raman bands for Mn–O lattice vibrations within the (2 × 2) tunnel structure of MnO6 octahedral are observed which confirm formation of nano-cryptomelane. The specific surface area (SSA) for nano-cryptomelane was calculated and equal to 299.03 m2/g while the surface fractal information (Ds) was 2.53. The process sensitivity to changes of H+ concentration is attributed to changes in structural elements-species distribution at the solid/aqueous interface. The pH optimum value was desired at pH 5 for exchange of Cs+ and/or Co2+ with K+ ions. The equilibrium studies show that Langmuir isotherm model was more fitted to the experimental data than that of Freundlich model.

Keywords  Nano-cryptomelane · Binary solution · Cobalt · Cesium · Sorption

Introduction
The amassing of hazardous metal ions through the food chain accompanied with a harmful effects for the human health thus to reduce these effects and for environmental protection, sequestration of these contaminants from wastewater is very important process. Estimation and removal of these toxic contaminants are essential to meet safety requirements and the environmental standards [1–3]. Both of cobalt and cesium ions are broadly utilized in the nuclear power plant and coal-fired power plants as well as in various applications of industry such as metallurgical, battery manufacturing, mining, electroplating, paints, grinding wheels, petroleum, pigments, and electronics [4–7]. Higher cobalt concentration has harmful impacts on the human beings; it leads to lung irritations, asthma, pneumonia, weight loss, paralysis, diarrhea, vomiting, damage thyroid hormone and liver and nausea[8–13]. Due to similarity of cesium-134 to sodium thus ingestion of cesium leads to its deposition in the soft tissues all over the body which in turn cause internal hazards[14–16].

Coagulation, evaporation, electrodialysis, chemical precipitation, chelation, reverse osmosis, membrane filtration, solvent extraction, biosorption, and ion exchange are various methods suggested for the elimination of toxic contaminants from wastewater [17–20]. Ion exchange process has several advantages more than other methods including high efficiency, cost-effectiveness, production of less toxic sludge, etc. [21, 22].

Several sorbent materials can be used for the elimination of these toxic contaminants from aqueous waste. Nano sized metal oxides (NMOs) have a high specific tendency for sorption of metal ions from liquid solutions; the most widely studied ones are aluminum oxides, titanium oxides, cerium oxides and manganese oxides. NMOs exist in different morphologies such as particles, tunnels and others. Both of size and shape of NMOs are important factors that affects greatly their sorption performance. Several efficient preparation procedures are widely studied to obtain a highly stable,
shape-controlled and mono disperse NMOs [23]. Nanosized manganese oxides (NMnOs) are widely studied for environmental concerns as birnessite and cryptomelane [24, 25].

Hydrous manganese oxide (HMO) and mixed-valence manganese oxides are most common NMnOs [23]. Mixed-valence manganese oxides considered as potential interesting sorbents for cations and usually present as octahedral molecular sieve (OMS). Cryptomelane considered as an example of mixed-valence octahedral molecular sieve (K-OMS-2) manganese oxide, the main oxidation states of manganese are Mn⁴⁺ and Mn³⁺ [23]. The OMS-2 group building unit is MnO₆ octahedral which in turn form a single octahedral chain through participating two opposite edges after that a double chain is resulted via combination of two neighbor single chains, finally, four chains corner connected forming a one-dimensional 2 × 2 open tunnel structure with a diameter of about 460 pm [26–28].

Cryptomelane has two ion exchange sites; particular sites found interior tunnel structure and the unspecific sites, ion exchanger outer surface sites. The exchangeable cation, K⁺, is located interior tunnel structure to stabilize negative charge balance that originating from Mn³⁺ in an otherwise perfect Mn⁴⁺O₂ structure. Several synthesis procedures have been published for synthesis of nano-cryptomelane such as sol–gel method [29] hydrothermal treatment procedure for birnessite [30] and oxidation of Mn²⁺ by KMnO₄, H₂O₂ or K₂S₂O₈ in acidic refluxing conditions [31]. Nano-cryptomelane considers as selective ion exchanger due to its porous and tunnel structure, hydrophobic nature and mixed valence of manganese [28].

The morphology of synthesized nano-cryptomelane (rod-like, fibrous-like and nest-like morphologies) depends incredibly on the preparation method (solid state, reflux and hydrothermal method) [32].

The previous work illustrated that nano-cryptomelane can be synthesized using several methods such as sol–gel route, hydrothermal treatment procedure of birnessite and oxidation of Mn²⁺ by KMnO₄, H₂O₂ or K₂S₂O₈ in acidic refluxing conditions. The main target of this work is utilization of synthesized nano-cryptomelane for retention of cesium and cobalt metal ions from single and binary solutions.

**Experimental**

**Materials and reagents**

Manganese sulfate, acetic acid and potassium permanganate, KMnO₄, were obtained from Alpha Chemika, Euromedex and El-Nasr Company for chemicals, respectively and used to prepare nano-cryptomelane. Cesium chloride and cobalt chloride were obtained from LOBA. NaOH and HCl were obtained from Fluka and used for pH adjustment.

**Preparation of nano-cryptomelane**

As mentioned in the previous work [28], the oxidation method was the selected procedure for preparation of nano-cryptomelane under acidic conditions [33]. The preparation method involved preparing 1.0 L of 0.2 M MnSO₄ in 2 M acetic acid. The acidified MnSO₄ was added over permanganate solution (0.35 M) pre-dissolved in 800 mL deionized water over a time period of 2 h at 65 °C in 4.0 L beaker with vigorous stirring. An aluminum hinder was used above the beaker and a hole was done to permit a thermometer to be inserted into the beaker. After 2 h, temperature was raised to 80 °C and held for about 10 min then a dark black manganese oxide was formed. The obtained mixture was gradually cooled until reach the room temperature and left overnight for the aging process after that wet-aged for 48 h at 7 °C. The resulted dark black MNos were centrifuged at 6000 rpm, washed many times using bi-distilled water and finally, freeze-dried for 8 days, Fig. 1.

**Removal studies**

10 mL of 10⁻³ M Co²⁺ or Cs⁺ metal ion solution was agitated with 0.05 g nano-cryptomelane and centrifuged to separate the liquid and solid phases. Same molar ratio (1:1) of Co²⁺ and Cs⁺ was used to prepare 10⁻³ M binary solution. The elemental analysis for the clear diluted liquid was approached using atomic absorption spectroscopy.

**Synthesis of multi-system solution**

A binary stock solution of 0.02 M ionic strength was prepared through dissolving same molar ratio, 1:1 of cesium and cobalt ions. The metal ion concentrations in the solutions were determined using an atomic absorption spectrophotometer (Buck Scientific) model 210 VGP, USA, an air-acetylene flame.

**Structural and surface area investigation of Nano-cryptomelane**

X-ray diffraction (XRD) results were determined by CuKα radiation at 40 kV using Schimadzo X-ray powder diffractometer and processed by using Match software. Raman-scattering data were performed at Raman shift between 100 and 3600 cm⁻¹ at room temperature with spectral resolution of 0.5 cm⁻¹, equipped using a Peltier-cooled charge-coupled device (1152 × 298 pixels). The excitation wavelength of the spectrum was 632.81 nm and was supplied using a He–Ne laser placed on an Olympus high-stability BXFM confocal microscope. Nitrogen adsorption–desorption isotherms of nano-cryptomelane were used for determination of SSA by
means of a fully automated surface area analyzer (Quantachrome Corporation, Nova station 2010 instrument, USA).

Brunauer–Emmett–Teller (BET) model can be given as [34]:

$$\frac{1}{V(\frac{P_0}{P} - 1)} = \frac{1}{C.V_m} + \frac{C - 1}{C - V_m} \cdot \frac{P_0}{P}.$$  \hspace{1cm} (1)

where $V$ refers to volume of adsorbed nitrogen at equilibrium pressure $P$ ($\text{cm}^3/\text{g}$), $P_0$ is the saturation pressure of nitrogen, $C$ is the characteristic constant. $V_m$ is volume of nitrogen of the monolayer coverage ($\text{cm}^3/\text{g}$), can be determined from slope and intercept of the linear fitting of the plot $1/\left[V(\frac{P_0}{P} - 1)\right]$ against the relative pressure $(P/P_0)$. Value of SSA was then determined from the calculated value of $V_m$, volume occupied by one mole of nitrogen gas and the sample mass and Avogadro's number[35]. In this work, modified Frenkel–Halsey–Hill (FHH) model [36] is adopted for estimating value of $D_s$ of sorbents using adsorption isotherm data. The logarithmic form for the modified (FHH) model can be described as follows:

$$\ln\left(\frac{V}{V_m}\right) = A \ln\left(\frac{P_0}{P}\right) + C.$$ \hspace{1cm} (2)

where $A$ is the power law exponent that is reliant in $D_s$ value and the adsorption mechanism. It is worth mentioning that when the pore surface dimension ($D_s$) is obtained, the relevant pressure ranged between 0 and 0.3. Then, the surface fractal information ($D_s$) value may be determined from the following equation:

$$D_s = 3 + A.$$ \hspace{1cm} (3)
Results and discussion

As mentioned in the past work, particle size of the synthesized nano-cryptomelane was ranged between 4 and 6 nm [28].

Structural investigation of nano-cryptomelane

X-ray diffraction analysis

XRD pattern for nano-cryptomelane is shown in Fig. 2a, the pattern reveals the existence of six diffraction peaks recorded at 2θ of 12.8°, 18.5°, 28.9°, 37.5°, 42° and 50° which are specific peaks for nano-cryptomelane [29, 37]. VESTA program was used to identify the crystalline structure of nano-cryptomelane, Fig. 2b.[38].

Raman spectroscopy

Raman scattering spectrum of nano-cryptomelane is illustrated in Fig. 3. Seven Raman bands are detected at 183, 286, 330, 386, 512, 574, and 753 cm\(^{-1}\) which are specific bands of the Mn–O lattice vibrations within the (2 × 2) tunnel structure of MnO\(_6\) octahedral [39]. The low-frequency Raman bands at 183 and 286 cm\(^{-1}\) are ascribed to an external vibration that derives from the translational motion of the MnO\(_6\) octahedral; the Raman bands at 330 and 386 cm\(^{-1}\) are specific to the Mn–O bending vibrations; The Raman bands located at 512 and 574 cm\(^{-1}\) may attributed to displacement of the oxygen atoms relative to the manganese atoms along the octahedral chains. The high-frequency Raman band at 753 cm\(^{-1}\) corresponds to the anti-symmetric Mn–O stretching vibrations.

Surface area measurements (SSA)

Figure 4a shows N\(_2\) adsorption–desorption isotherm of nano-cryptomelane. At low relative pressure region (P/P\(_0\) < 0.1), nano-cryptomelane display a steep uptake of nitrogen, on the other side at relatively higher pressure the hysteresis loop suggests N\(_2\) capillary condensation in mesopores, representing the existence of mesoporous structures in nano-cryptomelane [40]. Figure 4b shows the linear fitting for the plot of 1/[V\(_m\)(P\(_0\)/P − 1)] where V\(_m\) value was detected using the slope and the intercept data. The value the SSA compared to other scavengers was illustrated in Table 1. Value of D\(_s\) was calculated using slope of the fitting curve of plot of ln(V/V\(_m\)) versus ln(ln(P\(_0\)/P)) and detected to be 2.53.

Effect of initial effluent H\(^+\) ion concentration (pH)

The elimination efficiency of cesium and cobalt ions from single and binary solutions was studied at pH range of 1 to 6; the alkaline conditions were excluded to avoid complications of precipitation. The data reveals that sorption capacities of cesium and cobalt ions from single and binary systems increase with increasing pH of the effluent and the pH optimum value was 5.0, Fig. 5a. This may be attributed to the fact that at low pH values, a competition between H\(^+\) ions and cations for nano-cryptomelane exchange sites. The zero point charge of nano-cryptomelane, pHzpc, was detected and equal to 4.0. The surface of nano-cryptomelane possess a negative charge above pHzpc and positive below the pHzpc. Therefore, the sorption of cobalt and cesium ions at pH greater than 4 should be high, Fig. 5b. The relation
Fig. 3 Raman scattering spectrum of nano-cryptomelane

Fig. 4  a) N₂ adsorption/desorption isotherms of Nano-cryptomelane, b) Fitting curve for uptake of nitrogen of a monolayer coverage, and c) Fitting curve for surface fractal dimension
of Log $K_d$ as a function of pH was found to fit the following relations:

For Cs$^+$

a) Single solution Log $K_d = 0.6 \, \text{pH} - 2.1$, \hspace{1cm} (4)

b) Binary solution Log $K_d = 0.6 \, \text{pH} - 2.4$, \hspace{1cm} (5)

For Co$^{2+}$

a) Single solution Log $K_d = 0.5 \, \text{pH} - 2.2$, \hspace{1cm} (6)

b) Binary solution Log $K_d = 0.5 \, \text{pH} - 2.5$, \hspace{1cm} (7)

The slopes of the straight lines are corresponding to the valence of sorbed metal ions Fig. 5c. Values of $n$ for cesium and cobalt metal ions either in single solutions or in binary solutions were about 1 which reflects that both of them are sorbed as monovalent species. The speciation of Co$^{2+}$ and Cs$^+$ at different pH values in the aqueous solution are illustrated in Fig. 5d which illustrates that at the pH optimum value, pH 5, both of Co$^{2+}$ and Cs$^+$ are sorbed as monovalent species. Nano-cryptomelane has a higher affinity towards Cs$^+$ more than Co$^{2+}$ which may attributed to fact that the atomic radius of Co(OH)$^+$ is larger than that of Cs$^+$ thus the movement of monovalent cobalt species from the bulk of solution to the surface of nano-cryptomelane is slower than that of Cs$^+$[41, 42].

Effect of contact time and temperature

Corresponding to Figs. 7a and 8a and Tables 2 and 3 the experimental data indicate that sorption process more fitted to pseudo-second-order reaction which indicates that sorption process is chemisorption[44]. Sorption of Cs$^+$ and Co$^{2+}$ from single and binary solutions onto nano-cryptomelane was studied as a function of shaking time over time intervals of 1–180 min as shown in Fig. 6. Experimental data illustrate that the removal performance of Cs$^+$ and Co$^{2+}$ either from single or binary solutions increase by increasing the time of contact and equilibrium is obtained after about 45 min for all solutions. At beginning of the cation elimination process, the quantity sorbed increased rapidly which may be attributed to presence of more sorbing sites, after 45 min, equilibrium was obtained and sorbing sites are approximately saturated. Results show that the quantity sorbed of Co$^{2+}$ and Cs$^+$ increased with raising temperature which reflects the endothermic nature of sorption process. The percent of metal ion elimination may be detected using the following equation.

\[
\text{Elimination percent} = \frac{C_i - C_t}{C_i} \times 100,
\]

where $C_i$ and $C_t$ are metal ion concentration in solutions at the initial state and equilibrium time, respectively, (mg/L).

Experimental data were analyzed to determine rate constants of sorption reaction using the non-linear forms of pseudo-first-order Eq. (9) and pseudo-second-order kinetic models Eq. (10)[29].

\[
q_t = q_e \left(1 - e^{-k_1t}\right)^n,
\]

\[
q_t = \frac{k_2q_e^2t}{1 + k_2q_et},
\]

where $K_x$ is the rate constant, $x = 1$ pseudo-first-order, $x = 2$ pseudo-second-order, $q_e$ is the amount sorbed at equilibrium and can be determined as follow[43]:

| Material                         | SSA (m$^2$/g) | Sorption capacity (meq/g) | Measuring method | Particle size (µm) | Permanent negative charge, (meq/m²) | Refs  |
|---------------------------------|--------------|---------------------------|-------------------|------------------|------------------------------------|-------|
| Nano-cryptomelane              | 299.03       | 4.65                      | BET, Na-method    | 0.004–0.006      | 0.0155                             | This work |
| K-Birnessite                   | 16.3         | 1.8                       | BET, Na-method    | 0.8–1.5          | 0.11                               | [23]  |
| Amorphous manganese oxide      | 14.8         | 0.34                      | BET, N/A          | –                | 0.02                               | [39]  |
| Magnetically modified zeolite   | 25.15        | 0.82                      | Saturation*       | –                | 0.03                               | [40]  |
| Gismondite-type zeolite         | 10–13        | 2.25–2.37                 | –                 | 12–21**          | 0.18–0.23                          | [41]  |
| Treated natural zeolite         | 12.9–112     | 0.145–8.45                | Saturation*       | –                | 0.01–0.7                           | [42]  |
| Sepiolite (Si$_8$Mg$_8$O$_{29}$OH$_6$(OH$_2$)$_4$·8H$_2$O) | 17.34 | 0.12 | BET | – | 0.007 | [43] |
| Magnetic nano-zeolite           | 1380         | 4.44                      | BET, Na-method    | 0.038            | 0.003                              | [44]  |
| Mg/Fe hydroxalite              | –            | 0.089                     | Na-method         | 2–3              | –                                  | [45]  |

*aLangmuir monolayer saturation capacity

**D50 value

Table 1 Comparison of the SSA, sorption capacity, particle size, and permanent negative charge for different inorganic sorbents

*Langmuir monolayer saturation capacity

**D50 value
Fig. 5  

**a** Elimination efficacy. **b** Point of zero charge $P_{zpc}$ of nano-cryptomelane. **c** Effect of pH on sorption of a) Cs$^+$ b) Cs$^+$ (binary solution) c) Co$^{2+}$ d) Co$^{2+}$ (binary solution). **d** Species distribution of cobalt and cesium at room temperature.
Figures 7b and 8b indicate that the residual errors values from pseudo-first-order smaller than those of pseudo-second-order.

Freundlich, Eq. (12), and Langmuir, Eq. (15), isotherm models for multi-component sorption process were used to analyze the experimental data to describe the nature of the sorption sites.

where \( C_e, z \) is the equilibrium concentrations of the component \( z \), \( K_{F,z} \) is Freundlich constant for the component \( z \) indicating sorbent capacity, mg/g, (mg/L)\(^{1/n}\) and \( n \) is a constant describe the heterogeneity of the surface.

For the sorption of Co\(^{2+}\) and Cs\(^+\) in a binary system, Freundlich equation becomes;

\[
q_{e,Co} = K_{F,Co} \left( C_{e,Co}^{1/n_{Co}} + C_{e,Cs}^{1/n_{Cs}} \right). \tag{14}
\]

For the competitive sorption of metal ions from a multicomponent system, the extended Langmuir model given by the following equation:

\[
q_{e,x} = \frac{q_{m,x} b_x C_{e,x}}{1 + \sum_{y=1}^{N} b_y C_{e,y}}, \tag{15}
\]

where \( C_{e,x} \) and \( C_{e,y} \) are the equilibrium concentrations of the components \( x \) and \( y \), respectively, \( q_{m,x} \), mg/g, is the maximum monolayer sorption capacity for the component \( x \), \( q_{e,x} \) is the quantity sorbed of component \( x \), mg/g, at equilibrium in a multicomponent system, \( b_x \) and \( b_y \), L/mg, describe the affinity of sorbent towards the sorbates \( x \) and \( y \), respectively, \( y = 1, 2, 3, \ldots, N \), and \( N \) is the number of components in the experimental isotherm.

The extended Langmuir equation for the competitive sorption of Co\(^{2+}\) and Cs\(^+\) in a binary system becomes [45]:

\[
q_{e,Cs} = \frac{q_{m,Cs} b_{Cs} C_{e,Cs}}{1 + b_{Cs} C_{e,Cs} + b_{Co} C_{e,Co}}. \tag{16}
\]
The nonlinear fitting of the experimental data to Freundlich and Langmuir isotherm models are shown in Figs. 9 and 10 which illustrated that both models could represent the behavior of sorption process. The correlation coefficients of Langmuir are slightly higher than these of Freundlich model (Tables 4 and 5) [46, 47].

**Conclusion**

The performance of synthesized nano-cryptomelane for the sequestration of cobalt and cesium ions from their single and binary solutions was studied. The following specific conclusions could be drawn from the above mentioned investigations:

1. Nano-cryptomelane was prepared using oxidation method and the characteristic results indicated the formation.
2. The synthesized nano-cryptomelane possesses a tunnel structure with particle size ranged between 4 and 6 nm.
3. The XRD chart reveals existence of six diffraction peaks recorded at 2θ of 12.8°, 18.5°, 28.9°, 37.5°, 42° and 50° which are specific peaks for nano-cryptomelane.
4. Seven Raman bands are detected at 183, 286, 330, 386, 512, 574, and 753 cm⁻¹ which are specific bands of the Mn–O lattice vibrations within the (2 × 2) tunnel structure of MnO₆ octahedral.
(5) The SSA of nano-cryptomelane was determined and equal to 299.03 and $D_s$ was calculated and equal to 2.53.

(6) The pH optimum value for sequestration of cesium and cobalt ions was 5, the percent uptakes take the order $\text{Cs}^+ > \text{Co}^{2+}$.

(7) Kinetic studies illustrate that sorption process more fitted to non-linear pseudo-second-order model.

(8) Single system solutions show higher removal percentage of cobalt and cesium than that of the binary solution.

(9) This work recommends nano-cryptomelane as an effective sorbent material for the elimination of cobalt and cesium metal ions from single and binary solutions.

(10) Langmuir isotherm model fits the data reasonably well and it is more applicable than Freundlich isotherm.

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**Fig. 7** a Non-linear plot of pseudo-first-order kinetic model for sorption of $\text{Cs}^+$ and $\text{Co}^{2+}$ onto nano-cryptomelane at different temperatures. b Residual errors for non-linear regression of Kinetic data for cesium and cobalt in single and binary solutions in pseudo first order model.
Fig. 7 (continued)
Fig. 8  a Non-linear plot of pseudo-second-order kinetic model for sorption of Cs\(^+\) and Co\(^{2+}\) onto nano-cryptomelane at different temperatures. b Residual errors for non-linear regression of Kinetic data for cesium and cobalt in single and binary solutions in pseudo second order model
Fig. 8 (continued)
### Table 2 Regression parameters of $\text{Co}^{2+}$ and $\text{Cs}^+$ removal using pseudo first order kinetic model

|       | $\text{Cs}^+$ | $\text{Cs}^+ (\text{Cs}^++\text{Co}^{2+})$ | $\text{Co}^{2+}$ | $\text{Co}^{2+} (\text{Cs}^++\text{Co}^{2+})$ |
|-------|---------------|---------------------------------|----------------|---------------------------------|
| 298 K | $k_1, \text{min}^{-1}$ | 0.15 | 0.16 | 0.16 | 1.19 |
|       | $q_e, \text{exp. mg/g}$ | 23.78 | 11.18 | 11.18 | 4.78 |
|       | $q_e, \text{calc. mg/g}$ | 22.34 | 10.16 | 9.94 | 4.06 |
|       | $R^2$ | 0.83 | 0.87 | 0.87 | 0.51 |
|       | S.E | 1.02 | 0.61 | 0.61 | 0.31 |
| 303 K | $k_1, \text{min}^{-1}$ | 0.16 | 0.18 | 0.18 | 1.22 |
|       | $q_e, \text{exp. mg/g}$ | 23.99 | 11.23 | 11.23 | 4.80 |
|       | $q_e, \text{calc. mg/g}$ | 22.55 | 10.68 | 10.01 | 4.24 |
|       | $R^2$ | 0.75 | 0.85 | 0.85 | 0.51 |
|       | S.E | 1.16 | 0.36 | 0.36 | 0.27 |
| 313 K | $k_1, \text{min}^{-1}$ | 0.162 | 0.19 | 0.19 | 1.30 |
|       | $q_e, \text{exp. mg/g}$ | 24.32 | 11.25 | 11.25 | 4.81 |
|       | $q_e, \text{calc. mg/g}$ | 23.27 | 11.27 | 10.17 | 4.41 |
|       | $R^2$ | 0.66 | 0.82 | 0.82 | 0.50 |
|       | S.E | 1.28 | 0.37 | 0.37 | 0.28 |
| 323 K | $k_1, \text{min}^{-1}$ | 0.163 | 0.20 | 0.20 | 1.46 |
|       | $q_e, \text{exp. mg/g}$ | 24.50 | 11.27 | 11.27 | 4.82 |
|       | $q_e, \text{calc. mg/g}$ | 24.22 | 11.99 | 10.31 | 4.51 |
|       | $R^2$ | 0.52 | 0.80 | 0.80 | 0.59 |
|       | S.E | 2.36 | 0.37 | 0.37 | 0.29 |

### Table 3 Regression parameters of $\text{Co}^{2+}$ and $\text{Cs}^+$ removal using pseudo second order kinetic model

|       | $\text{Cs}^+$ | $\text{Cs}^+ (\text{Cs}^++\text{Co}^{2+})$ | $\text{Co}^{2+}$ | $\text{Co}^{2+} (\text{Cs}^++\text{Co}^{2+})$ |
|-------|---------------|---------------------------------|----------------|---------------------------------|
| 298 K | $k_1, \text{min}^{-1}$ | 0.009 | 0.02 | 0.02 | 0.22 |
|       | $q_e, \text{exp. mg/g}$ | 23.78 | 11.18 | 11.18 | 4.78 |
|       | $q_e, \text{calc. mg/g}$ | 24.57 | 11.67 | 11.36 | 4.63 |
|       | $R^2$ | 0.87 | 0.82 | 0.90 | 0.69 |
|       | S.E | 0.88 | 0.74 | 0.22 | 1.04 |
| 303 K | $k_1, \text{min}^{-1}$ | 0.010 | 0.05 | 0.021 | 0.24 |
|       | $q_e, \text{exp. mg/g}$ | 23.99 | 11.23 | 11.23 | 4.8 |
|       | $q_e, \text{calc. mg/g}$ | 24.77 | 11.93 | 11.45 | 4.78 |
|       | $R^2$ | 0.84 | 0.65 | 0.89 | 0.69 |
|       | S.E | 0.92 | 0.76 | 0.34 | 0.25 |
| 313 K | $k_1, \text{min}^{-1}$ | 0.011 | 0.06 | 0.022 | 0.28 |
|       | $q_e, \text{exp. mg/g}$ | 24.32 | 11.25 | 11.25 | 4.81 |
|       | $q_e, \text{calc. mg/g}$ | 24.96 | 12.31 | 11.55 | 4.90 |
|       | $R^2$ | 0.81 | 0.8 | 0.88 | 0.73 |
|       | S.E | 0.95 | 0.78 | 0.34 | 0.25 |
| 323 K | $k_1, \text{min}^{-1}$ | 0.013 | 0.10 | 0.02 | 0.28 |
|       | $q_e, \text{exp. mg/g}$ | 24.50 | 11.27 | 11.27 | 4.82 |
|       | $q_e, \text{calc. mg/g}$ | 24.98 | 12.33 | 11.65 | 5.01 |
|       | $R^2$ | 0.77 | 0.66 | 0.87 | 0.66 |
|       | S.E | 0.86 | 0.70 | 0.34 | 0.26 |
Fig. 9 Non-linear plot of Freundlich isotherm plots for sorption of Cs\(^+\) and Co\(^{2+}\) onto nano-cryptomelane at different temperatures
Fig. 10  Non-linear plot of extended Langmuir isotherm plots for sorption of $\text{Cs}^+$ and $\text{Co}^{2+}$ onto nano-cryptomelane at different temperatures
Table 4 Freundlich parameters for sorption Co$^{2+}$ and Cs$^+$ onto nano-cryptomelane at different temperatures

| Temperature | $1/n$ | $k$, mg/g | $R^2$ | $R^2$ |
|-------------|-------|------------|-------|-------|
| 298 K       | 0.347 | 0.364      | 0.430 |       |
| 303 K       | 0.344 | 0.369      | 0.434 |       |
| 313 K       | 0.354 | 0.370      | 0.440 |       |

Table 5 Extended Langmuir parameters for sorption Co$^{2+}$ and Cs$^+$ onto nano-cryptomelane at different temperatures

| Temperature | $Q_0$, mg/g | $b$, mg/mg | $R^2$ | $R^2$ |
|-------------|-------------|------------|-------|-------|
| 298 K       | 116.10      | 0.044      | 0.048 | 0.071 |
| 303 K       | 120.72      | 0.048      | 0.049 | 0.072 |
| 313 K       | 127.27      | 0.0480     | 0.050 | 0.074 |

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