Performance evaluation of zirconium silicate composite for removal of cadmium and zinc ions

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Abstract

The purification of wastewater is preferred using the adsorption technique by the column due to the high efficiency of the process. The column studies are achieved to predict the removal of pollutants and clarify the adsorption capability of these pollutants in the treatment process of wastewater. Zinc and cadmium ions are presented in both radioactive and industrial wastes. Consequently, this work focused on the removal of zinc and cadmium ions from polluted wastewater using a fixed-bed column. Zirconia–silicate composite (ZrO$_2$–SiO$_2$) was produced using the sol-gel technique and analyzed for this purpose. Various parameters as bed depth (2, 3, and 5 cm), flow rate (2 and 3 mL/min), and initial ions concentrations (50-200 mg/L) were investigated. The column performance was computed to be 80.3 and 79.3% for Zn$^{2+}$ and Cd$^{2+}$, respectively, at the optimum conditions (3 cm bed depth, 2 mL/min flow rate, and 100 mg/L ions concentration). Thomas, Adams–Bohart, and Yoon–Nelson models were performed to estimate the breakthrough curves and compute the column model parameters which are valuable for process design. Thomas model presented the highest $R^2$ values (0.84-0.97) and offered the most accurate estimation of the adsorption process.

Keywords: Fixed-bed column; adsorption; modeling; zinc and cadmium.
1. Introduction

Cadmium and zinc ions are presented in both radioactive and industrial wastes. Cadmium has numerous radioisotopes, including $^{109}$Cd (half-life $\approx 462.9$ days) which is utilized in nuclear reactors as a shield and control rod for neutron absorption [1]. It possesses also an important role in some industries as alloys, batteries, aerospace coatings, stabilizers, and plating [2]. In environmental systems, it mostly presents as Cd(I) and Cd(II), but the latter exists in higher concentrations. Cadmium is a markedly toxic metal and has a very low biocidal dose for mammals, which could damage the lungs, liver, and kidney [2]. Therefore, the capture of cadmium from the water source is substantial to the environment clean from pollution and human health [3]. Zinc has several radioisotopes, including $^{65}$Zn ($t_{1/2} \approx 244.2$ days), it is widely employed in agricultural, medical, and biomedical research; it is also utilized for industrial purposes [4]. In environmental investigations, zinc pollution is evaluated by comparing the isotopic signature of point sources as waste incinerator residues and fumes, tire wear, and industrial outcomes as electroplated hardware. The quantity of zinc released to the environment has clearly enlarged proportionally to its industrial consumption; therefore, zinc ions should be captured from wastewater.

Different methods were used to treatment of wastewater streams contaminated by cadmium and zinc ions; these methods comprise ion exchange, chemical precipitation, adsorption, membrane filtration, solvent extraction, flotation, coagulation-flocculation, and electro-dialysis. Adsorption is one of the prominent methods for capture of pollutants from wastewater streams [5]. It is an effective, low-cost technique, and has the simplicity of operation than other techniques employed in the capture of ions [6, 7]. The purification of wastewater is preferred using the adsorption technique by column due to high efficiency of the process. The column studies are achieved to predict the capture of ions and clarify the adsorption ability of these ions in the treatment process of wastewater [8].
Several materials had been synthesized and employed to scavenge various ions from wastewater streams. The stability of inorganic sorbents makes it desirable than organic sorbents. Also, the inorganic materials were successfully utilized in the immobilization step of waste elements prior to the disposal step comparing to organic materials [9]. Various inorganic sorbents were promised to capture toxic pollutants from wastewater stream [10-16]. Metal oxides are extensively employed for the treatment of hazardous waste. Generally, the characteristics of oxides strongly affect the sorption behavior [9]. Zirconia (ZrO$_2$) is employed as a sorbent material in many works, because of the selectivity behavior towards multivalent anions (such as phosphates, arsenates, arsenites, etc.) [17-20]. Also, zirconia is distinguished by different features such as it is insoluble material, non-toxic, chemically stable, and good resistance to acids, oxidants, and alkalis [21]. ZrO$_2$ has a small surface area. This influences the behavior of it; therefore the SiO$_2$ was added to ZrO$_2$ to improve its chemical and physical properties [22, 23].

In this study, zirconia–silicate composite (zirconium silicate) was synthesized and investigated as a sorbent material for the capture of cadmium and zinc ions from wastewater streams using column the technique. Zirconia–silicate composite was characterized using different analytical techniques such as SEM, XRD, FTIR, and thermal analysis. Also, the influences of bed height, flow rate, and initial ion concentration have been investigated.

2. Experimental

2.1. Chemicals and synthesis of zirconia–silicate composite

The stock solutions of Cd$^{2+}$ and Zn$^{2+}$ were prepared by dissolving a quantity of anhydrous zinc chloride (Merck,98%), anhydrous cadmium chloride (Sigma-Aldrich, 99%) in distilled water. Zirconium chloride and silicon tetrachloride are used as precursors. The initial pH was attuned to the desired values to the following experimental using 0.01M HCl and/or
0.01 M NaOH solutions. The zirconia–silicate composite was synthesized via the sol-gel technique as exemplified in the previous work [20, 24, 25].

Preparation of zirconia–silicate inorganic composite (ZrO2-SiO2) through the sol-gel hydrolysis process is established involving the production of resin between formaldehyde and urea in the existence of SiCl4 and ZrCl4 as precursors. Preparation of ZrO2-SiO2 is built on incorporation of SiCl4 and ZrCl4 in the structure of urea–formaldehyde resin under certain conditions of time, temperature, and pH as follows; reflux mixture of formaldehyde and urea (ratio 2:1) at pH 8.5 for 1.0 h with stirring for polymer formation. The polymerization reaction (resin formation) was terminated by adding ethylene glycol to the mixture after 1.0 h to gain a clear transparent gel. Then adding zirconium and silicon tetrachloride (1:1) to the gel, the pH was attuned at 1.0–2.0 at a temperature of 85°C then refluxing them for 2.0 h with continuous stirring. A viscous white gel was formed. Withdraw the excess water using a pump. Drying the gel at 75°C was occurred for 24 h to strip the excess water molecules. To completely remove the urea–formaldehyde, calcination was achieved at 850°C in the air for 2.0 h. the produced white powder of ZrO2-SiO2 is already to use. The proposed mechanism of the preparation process is illustrated by Fig. 1.

2.2. Characterization of ZrO2-SiO2 composite

The prepared ZrO2–SiO2 was characterized using different analytical techniques. Scanning Electron Microscope (SEM) was employed to explore the surface morphology of the sample by SEM, JEOL, JEM 1000CX. X-ray Diffraction(XRD) analysis displays the most comprehensive description of components of the material. ZrO2–SiO2 was characterized using CuK radiation by Shimadzu X-ray Diffractometer. The thermal analysis measurements were executed by TGA/DTA, Shimadzu, Japan. Known sample weight was put in a crucible and its dehydration/combustion was achieved from room temperature to 1000°C for composite
powder at a heating rate 20°C/min. Fourier Transformed Infrared Spectroscopy (FTIR) was employed to define the IR radiation absorption by samples using PerkinElmer,BX spectrometer.

2.3. Batch studies

The impact of pH on adsorption of Cd²⁺ and Zn²⁺ ions on the prepared zirconium silicate powder was followed up using of batch technique by shaking series of 10mL of 100 mg/L solutions of Cd²⁺ and Zn²⁺ with 0.1 g of ZrO₂–SiO₂ at different pH values (1 to 7) for overnight at 25°C. After equilibration, the mixtures were centrifuged to separate the two phases, then the ions concentration in the queues phase was determined by atomic-absorption-spectrophotometer (BuckScientific) model 210VGP, USA. The removal percent (R%) and the quantity of ions adsorbed onto ZrO₂–SiO₂ (qₑ, mg/g ) were computed by the following Eqs.

\[ R\% = \frac{C_o - C_e}{C_o} \times 100 \]  

\[ q_e = (C_o - C_e) \times \frac{V}{m} \]  

(1)

(2)

where \( C_e \) and \( C_o \) (mg/L) give ions concentrations after and before the adsorption, respectively, V(mL) is the sample volume, and \( m \) (g) is the sorbent mass.

2.4. Fixed-bed column investigation

A glass column of 10.0cm length and 1.0cm of internal diameter was utilized. It was packed by ZrO₂–SiO₂ sample with various bed depths (2, 3, and 5 cm). Glass wool was located at the column end to avoid any missing powder. The composite was pretreated using deionized water at pH =6.0±0.1 and room temperature (25°C). Feed solutions comprise Cd²⁺ and/or Zn²⁺ ions were fed to the column by a peristaltic pump through different flow rates (2 and 3 mL/min) at room temperature. The Cd²⁺ and Zn²⁺ ions solutions were collected from
the column end in the fraction collector. The ions concentration was specified by the Atomic Absorption Spectrophotometer. The breakthrough and the exhaustion times are gained at effluent concentration ≈5 and ≈95% of the influent concentration, respectively [26]. The breakthrough capacity(mg/g) of ions was computed as follows [27]:

\[\text{Capacity} = \frac{\frac{1}{2} V x C_o}{m}\]  \hspace{1cm} (4)

where \(V_{1/2}\) is the volume (liter) at which the ions concentration is 50%, \(C_o\) is the initial ion concentration(mg/L) and \(m\) is the mass(g).

The total quantity of ions adsorbed (\(q_{tot}\), mg) at a feed concentration of \(C_o\), mg/L, and a flow rate \(Q\), mL/min, are estimated by measuring the area under the breakthrough curve(A) that gained by the integration of sorbed ions concentration \([C_{ads} = (C_o - C)\), mg/L] against time plot as clarified by Eq. (5) [28]:

\[q_{tot} = \frac{QA}{1000} = \frac{Q}{1000} \int_{t=0}^{t=t_{tot}} C_{ads} \, dt = \frac{Q}{1000} \int_{0}^{t=t_{tot}} (C_o - C) \, dt \]  \hspace{1cm} (5)

where \(t_{tot}\) is the total time of flow(min). The total quantity of the Cd\(^{2+}\) and Zn\(^{2+}\) ions fed to the column(\(m_{tot}\), mg) is computed as follows:

\[m_{tot} = C_o \frac{V_{eff}}{1000}\]  \hspace{1cm} (6)

where \(V_{eff}\) is the effluent volume(mL). The total ions removal (the column performance, \%) is computed as follows [29]:

\[\text{Total metal ion removal(\%) = } \frac{q_{tot}}{m_{tot}} \times 100\]  \hspace{1cm} (7)
3. Results and Discussion

3.1. Characterization of ZrO$_2$–SiO$_2$ composite

3.1.1. FTIR analysis

The FTIR spectrum of ZrO$_2$–SiO$_2$ is displayed in Fig. 2. The peaks located at 469.78 and 829.06 cm$^{-1}$ explain the overlapping of the bending vibrations of Si–O and M–O groups from the Si–O–Si and Si–O–M bonds. Bands at 1041.44–1097.18 cm$^{-1}$ are produced from the asymmetric vibrations bands of the Si–O and Zr–O bonds. These bands confirm the incorporation of the zirconium ions into silica structure (the asymmetric vibrations of Si–O–Si bonds of pure silica occur at a wavenumber value $\approx$1096 cm$^{-1}$ and the shift to a lower wavenumber illustrated that quantity of the incorporated metal increases). The bending vibration bands indicated at 1560.74 and 1630.09 cm$^{-1}$ are characteristic of the adsorbed water molecules. The stretching vibrations peaks that appeared at 2847.87–3385.15 cm$^{-1}$ are concerning to the bridging OH groups [30]. The absence of the peaks of Si–OH and Zr–OH groups that appear at wavenumber ranged 4000–3700 cm$^{-1}$ confirm that zirconium was incorporated into the silicate structure. [31].

![Fig. 2](image)

3.1.2. X-ray Diffraction analysis

The XRD of zirconia-silicate sample displays broadband ranged between $2\theta$=25–35° and also, several amorphous materials (Fig. 3). The broadband approves the existence of small particles in the macro-size [30].

![Fig. 3](image)

3.1.3. Scanning Electron Microscope

The SEM photograph of ZrO$_2$-SiO$_2$ is obtainable in Fig. 4. The SEM photograph of zirconia-silicate composite is classified by the appearance of spherical particles with variable...
sizes ranged from 1–5 µm, the more significant size is 2 µm. The microstructure of particles without observed agglomeration illustrated the compact and homogeneous distribution of zirconium and silicate particles. The figure shows that ZrO₂–SiO₂ material is quite porous which simplifies the adsorption of Cd²⁺ and Zn²⁺ ions.

Fig. 4

3.1.4. Thermogravimetric analysis

DTA patterns of zirconia-silicate composite are obtainable in Fig. 5. Two main endothermic peaks appear; the first one occurs at 76.08 °C, corresponding to water molecules that are physically adsorbed on zirconia-silicate composite [32]. The second peak at 282.02 °C arises from the strongly adsorbed water onto the sample. The TGA line displays the weight loss of two stages. The initial stage covers the range between 70–250°C losses of about 6.06% of the net weight due to dehydration. With increasing the temperature up to 600°C the sample lost 3.96% and the total weight loss was 10.02% as outlined in the figure.

Fig. 5

3.2. Effect of pH

The batch investigation was designed to specify the optimum pH for cadmium and zinc ions adsorption onto ZrO₂–SiO₂ composite. The effect of pH is a substantial factor that often impacts the capture of sorbate from the solution. Figure 6 reveals that the ions adsorption was increased by increasing the pH. To avoid the precipitation of ions as hydroxides, pH above 7 was not applied [33, 34]. At low pH, the adsorbent surface has excess hydronium ions(H₃O⁺), hence adsorption of Cd²⁺ and Zn²⁺ cations is restricted. With increasing pH, the H₃O⁺ ions decreased, consequently, the cations are easily adsorbed by zirconia-silicate composite. Hence, the rise of adsorption with increasing the pH is noted in agreement with the literature [35-37]. The pH was desired at pH 6.0 to be the optimum value at which the percent uptake of
Zn²⁺ and Cd²⁺ was 90.5 and 69.1 %, and the quantity adsorbed was 9.05 and 6.91 mg/g, respectively, as displayed in Fig. 6.

3.3. Fixed-bed column studies

The efficiency of bed depth is achieved via the notion of breakthrough curves. The volume or time for breakthrough occurrence and its shape are essential features for estimating the operation and dynamic response of the sorption column. When the sorption zone moves up and the upper portion of this zone reaches the column top, the effluent concentration begins to increase rapidly; this is named the breakthrough point. Some parameters were studied as follows.

3.3.1. Effect of bed depth

The bed height is utilized to assess the adsorbent materials for the continuous flow of liquid waste on an industrial scale. The breakthrough curves gained for Cd²⁺ and Zn²⁺ adsorption onto ZrO₂–SiO₂ at several bed depths (2, 3, and 5 cm) for a constant linear flow rate equals 2 mL/min and at 100 mg/L initial Cd²⁺ and/or Zn²⁺ concentrations are displayed in Fig. 7. The results explored that the breakthrough volume varies with bed depth. The capacity and percent removal (column performance) of both Cd²⁺ and Zn²⁺ rose with raising bed height as denoted in Table 1. This raise is due to the rise of adsorbent doses in higher beds, which supplies greater adsorption sites for both ions. The breakthrough time of Zn²⁺ adsorption was 44, 72, and 104 min at depths of 2.0, 3.0, and 5.0 cm, respectively. While for Cd²⁺, the breakthrough time was 36, 44, and 64 min at bed height of 2.0, 3.0, and 5.0 cm, respectively. These results outlined that the breakthrough time rose with raising the bed height. Similarly, the exhaustion time for both ions rose with the raise of bed height, this is essentially assigned to the increased adsorption sites and longer interaction time as the depth increased. The outcomes are denoted by Table 1.
3.3.2. Effect of initial ion concentration

Effect of varying the initial Cd$^{2+}$ and/or Zn$^{2+}$ concentrations (from 50 to 200 mg/L) at a flow rate of 2.0 mL/min and depth of 3.0 cm are explored in Fig. 8. The removed quantities of Cd$^{2+}$ and/or Zn$^{2+}$, column performance, and capacity were assessed from the adsorption outcomes as denoted by Table 1. The outcomes revealed that with the growth of initial Cd$^{2+}$ and/or Zn$^{2+}$ concentration, the solution volume treated before breakthrough decreases considerably. This is caused by that the high ion concentration easily saturates the column bed, thereby declining the breakthrough time. Higher adsorbed quantities were gained at higher ion feed concentrations [38]. The essential driving force of the adsorption process may be the concentration variance between the ions in the aqueous and adsorbent.

3.3.3. Flow rate effect

The flow rate effect on Cd$^{2+}$ and Zn$^{2+}$ adsorption by ZrO$_2$–SiO$_2$ was investigated by varying the flow rate from 2 to 3 mL/min and keeping the concentration at 100 mg/L and bed depth of 3 cm. The plots of breakthrough curves of Cd$^{2+}$ and Zn$^{2+}$ at various flow rates are explored in Fig. 9. The total adsorbed ion quantities and the ion removal percentage were assessed from the adsorption data and are denoted by Tables 1. As is evident from these outcomes, the flow rate acceleration minimizes the volume treated efficiently until breakthrough and thereby reduces the service time of the bed. This is caused by the decrease in the residence time of both ions within the bed at higher flow rates. Much sharper breakthrough curves for Cd$^{2+}$ and Zn$^{2+}$ adsorbed onto ZrO$_2$-SiO$_2$ were gained at higher flow rates.
rates. The quantity of Cd\(^{2+}\) and Zn\(^{2+}\) adsorbed and breakthrough time also reduced with raising flow rate. This is certainly caused by the reduced contact time leads to a low distribution of the adsorbate inside the bed [39]; this causes lower ions diffusion among the ZrO\(_2\)–SiO\(_2\) particles.

**Fig. 9**

### 3.4. Breakthrough curves modeling

The design of industrial adsorption structure involves the investigation of numerous factors that is achieved in the laboratory; this involves high investment and consumes a significant period of time. Therefore, modeling is utilized as alternative methods to assess the kinetic parameters of adsorption in a continuous flow column and applied in the scale-up process from lab scale to the industrial scale. Development of a model which explores such concentration–time profile is difficult in most cases, since the ion concentration, which transfers across the bed, continuously varies and, hence, the process does not run at a steady state. The essential models for a fixed–bed column are attributed to the mechanism responsible for the method (transfer of mass from the solute to the solid surface, diffusion and/or interaction on the solid surface) and contain mass balances amid the fluid and solid and for the adsorbed solute, process rate, etc. In this investigation, various simple mathematical models as Thomas, Yoon and Nelson, and Adams–Bohart models are applied.

#### 3.4.1. Thomas Model

Thomas equation is generally and widely applied in the column system. It is suitable for estimating the continuous-flow column capacity and breakthrough curves. The basic limitation of Thomas theory is: the adsorption is not controlled by chemical interaction but by mass transfer at the interface [1, 40]. The Thomas linear formula is stated as follows [41].
\[
\ln \left( \frac{C_o}{C_t} - 1 \right) = \frac{mq_{Th} k_{Th}}{Q} - C_o k_{Th} t \tag{12}
\]

where \( k_{Th} \) is the Thomas rate constant (mL min\(^{-1}\) mg\(^{-1}\)) and \( q_{Th} \) is the adsorption capacity (mg/g), \( m \) gives the mass of adsorbent (g) and the time is expressed by \( t \) (min). The \( k_{Th} \) and \( q_{Th} \) values were computed from the plot of \( \ln(C_o/C_t) - 1 \) against \( t \). The predicted breakthrough curves are explored by Fig. 10 (a–c). The \( k_{Th} \) values were reduced with the rise of influent concentration and bed depth and rose with the rising of flow rate as denoted by Table 2. This is resulting from that a higher feed concentration reduces rate of the mass transfer by increasing the contact time between the adsorbate and adsorbent, therefore, the \( k_{Th} \) reduced by raising the feed concentration. The \( k_{Th} \) value was reduced by the raising of bed height representing a reduced reaction rate due to a longer contact time for higher bed depth. The \( k_{Th} \) values increased at high flow rates as a result of a high mass transfer rate. While for the capacity, \( q_{Th} \), as the feed concentration raises the \( q_{Th} \) value raises, due to the driving force for the transfer of mass which enhances the capacity. The values of \( q_{Th} \) increased also by raising the bed depth, this is caused by the increased adsorption sites and longer contact time. While \( q_{Th} \) was reduced by raising the flow rate due to insufficient time for the adsorption process. These outcomes are in agreement with those denoted in the literature [42, 43]. The regression coefficient values, \( R^2 \), are in the range 0.84–0.97 for both ions, this outlines that the breakthrough curve simulation is well predicted by Thomas model.

Fig. 10

Table 2
3.4.2. Yoon–Nelson Model

Nelson and Yoon established a simple model handling the breakthrough of sorbate. The model does not involve information about features of the system as kind of the adsorbent and the physical features of the adsorption bed. It is expressed by Eq. (13) [44].

\[
\ln \left( \frac{C_t}{C_o - C_t} \right) = k_{YN} t - k_{YN} \tau
\]  \hspace{1cm} (13)

\[
q_{YN} = \frac{1}{2} \left( \frac{C_o Q 2\tau}{m} \right) = \frac{C_o Q \tau}{m}
\]  \hspace{1cm} (14)

where, \( k_{YN} \) is the rate constant, min\(^{-1}\), \( \tau \) gives the time to reach 50% of the feed concentration, min. They can be computed from the intercept and slope of plotting \( \ln[(C/C_o-C)] \) against \( t \), Fig. 11. The adsorption capacity, \( q_{YN} \), can be computed using Eq. (14).

Table 3 denotes the parameters values of Yoon-Nelson model. The \( q_{YN} \) values rose with rising both the concentration and bed height and reduced by rising the flow rate. While, the \( k_{YN} \) value reduced with the rising of both bed depth and influent concentration, and rose with raising the flow rate. The explanations of these behaviors are illustrated above. The time required to reach 50% of the retention, \( \tau \), rose with raising the bed depth resulting from the binding sites increase and longer contact time. While raising the influent Cd\(^{2+}\) and Zn\(^{2+}\) concentrations significantly reduced the \( \tau \) value due to the rapid saturation process, and \( \tau \) decreased as the flow rate rose because the adsorption sites being occupied earlier at a high flow rate. Table 3 indicates that the computed \( \tau \) and \( q_{YN} \) values are not similar to the experimental outcomes and by comparing the \( R^2 \) values, Thomas model exhibited higher \( R^2 \) values (0.84-0.97) than Yoon-Nelson model This recommends that Thomas model offers a more accurate estimation of the Cd\(^{2+}\) and Zn\(^{2+}\) adsorption onto ZrO\(_2\)–SiO\(_2\) composite in a fixed-bed column.
3.4.3. Adams–Bohart Model

Dynamics of the sorption process have been studied using the bed depth service time (BDST) method based on a model proposed by Adams and Bohart [45]. This model supposed that the rate is proportional to the remaining capacity of adsorbent and the adsorbate species concentration. Adams–Bohart model is applied only for explanation of the first portion of breakthrough curve, 10–50% of saturation points. According to Adams–Bohart model, the following formula is gained.

\[
\ln \left( \frac{C_t}{C_o} \right) = k_{AB} C_o t - k_{AB} N_o \frac{Z}{F}
\]  \hspace{1cm} (15)

where \(k_{AB}\) is the kinetics constant in L mg\(^{-1}\) min\(^{-1}\); it is defined as the solute mass transfer rate from the fluid to the solid phase and proportional to the flow rate. \(N_o\) gives the concentration in solid phase, mg/L, \(C_t\) donates the concentration in the liquid phase, mg/L, \(C_o\) is the influent concentration, mg/L, \(F\) is the linear flow rate, cm/min, and \(Z\) gives the bed depth, cm. The \(N_o\) and \(k_{AB}\) values can be computed from plotting \(\ln(C_t/C_o)\) against \(t\) as explored by Fig. 12 and Table 4. Adams–Bohart theory reproduces satisfactorily the initial portion of the breakthrough curve for the used concentrations. As the feed concentration increases, the concentration in solid phase increases, however, the \(k_{AB}\) value decreases as the concentration increases. These results agree with other researchers studying different solute–adsorbent systems [46–48].
Table 4

Conclusion

Zirconia–silicate composite (ZrO$_2$-SiO$_2$) was successfully synthesized utilizing the sol-gel method, and then used to remove Cd$^{2+}$ and Zn$^{2+}$ by fixed-bed column technique. The capacity of continuous-flow column and breakthrough-curves were predicted using different models. Yoon-Nelson, Thomas, and Adams–Bohart models successfully reproduce the breakthrough-curves, due to the equivalence of the mathematical expressions. Nevertheless, Thomas theory is preferred since it provides more data about the adsorbent physical characteristics. These outcomes indicated that ZrO$_2$–SiO$_2$ composite adsorbent is an attractive material for the capture of Cd$^{2+}$ and Zn$^{2+}$ using the fixed-bed column.

Conflict of Interest

The authors declare no conflict of interest

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