A porous material of cross-linked adenine-polyethylene glycol diglycidyl ether for copper ion adsorption

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Abstract
A porous material (PEA) was prepared by the ring opening polymerization of polyethylene glycol diglycidyl ether with adenine in a simple sol-gel method. The structure and composition of PEA were characterized by SEM, FT-IR, BET and XRD. The adsorption experiments of copper ion by PEA at different pH, temperature, contact time and initial concentration were studied. The results show that the PEA is macroporous, the optimum adsorption pH is 5 and the saturated adsorption time is 180 min. The maximum equilibrium adsorption capacity of copper ion is 80.1 mg g−1 at 40 °C according to the Langmuir model and the competitive adsorption test shows that PEA has good adsorption on copper ion, but low effect on cobalt, cadmium and nickel. The repeated adsorption experiments show that PEA could still adsorb 82% of the first adsorption capacity after 5 times elution. These results indicate that the PEA can be used as a practical adsorbent for copper ion adsorption in aqueous solution.

1. Introduction

With the development of industry and society, environmental pollution has become increasingly serious. Heavy metals (such as copper, cadmium, zinc, lead) pose a serious threat and far-reaching influence to human health due to its high toxicity, persistence and bio-enrichment effect [1–5].

The treatment methods of heavy metal pollution include chemical precipitation, flocculation, membrane filtration, ion exchange, biological method, electrochemistry method and adsorption [6–10]. Due to the easy operation, renewability of adsorbents and economic feasibility, adsorption has become a widely studied and applied method for heavy metal treatment [11]. The adsorption property of adsorbent is dominated by the physical and chemical properties, which include pore size distribution, specific surface area and the species and density of their functional groups [12].

Adenine is a kind of natural nitrogen heterocycle which exists naturally in nucleotides. Adenine contains many nitrogen atoms that can be used for coordination, it has been studied in supercapacitors [13], adsorption [14] and other areas. Using the self-assembling reaction of adenine and complementary tricarboxylic acid derivatives, Sukula P K et al [14] synthesized an adenine based bicomponent hydrogels (AND-tpca), which has a high adsorption capacity of crystal violet dye reaching 600 mg g−1. The special performance of MOFs makes them become the focus of recent research in the field of environmental adsorption. Using zinc ions, adenine and carboxyl ligands as raw materials, Xie and co-workers [15] prepared a cationic metal-organic framework (ZJU-48), whose pore structure is one-dimensional pores of about 9.1 × 9.1 Å2. The ZJU-48 has good stability in water for about one week and high adsorption capacity towards methylene blue dye of 582.44 mg g−1. These
performance and regeneration make ZJU-48 an adsorbent with application prospect. And even more subtly, by grafting the nucleobase adenine to a highly porous metal-organic framework (MOF), Mithun Sarker et al utilized the MOFs to remove nitrogen-containing compounds (such as indole and quinolone) from a model fuel by adsorption [16]. Although there have been many studies on the use of adenine for environmental adsorption, to the best of our knowledge, there is no research on the adsorption of heavy metals using adenine.

Polyethylene glycol diglycidyl ether (PEGDE) is well known of their reactivity to amino and hydroxyl groups. It is made from polyethylene glycol, which is considered to be non-toxic and hydrophilic, by epoxy functionalization [17, 18]. Such as, by crosslinking β-cyclodextrin with PEGDE, Hiroyuki Kono and co-workers constructed a series of water-insoluble cyclodextrin polymers with high encapsulation performance toward bisphenol A in aqueous media [18]. PEGDE can be prepared into different kinds of adsorbents, Ali H. Jawad and co-workers prepared a cross-linked biofilm with chitosan and PEGDE. The biofilm showed high adsorption capacities of 165.3 mg g⁻¹ and 131.2 mg g⁻¹ toward reactive red 120 and methyl orange, respectively [19]. Therefore, PEGDE can be considered as a kind of material for preparing porous adsorbent with good adsorption capacity and hydrophilic.

Herein, by using the PEGDE as the framework, adenine as the functional monomer, a new kind of polyethylene glycol diglycidyl ether-adenine porous adsorbent (PEA) was successfully designed and prepared. The FT-IR, SEM, XRD and BET were performed to study its structure and micromorphology. Besides, the adsorption properties of the PEA toward Cu²⁺ in aqueous solution were investigated and analyzed, including effect of pH (2 to 6), adsorption isotherm, adsorption kinetics, reusability and competitive adsorption among Cu²⁺, Cd²⁺, Co²⁺ and Ni²⁺. Moreover, the mechanism was also discussed.

2. Experimental sections

2.1. Materials
Nitrates or halides of the four heavy metals, which are Cu²⁺, Cd²⁺, Co²⁺ and Ni²⁺, were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Adenine and PEGDE whose average molecular weight is 500 were also purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Dimethyl sulfoxide (DMSO), hydrochloric acid (HCl), sodium hydroxide (NaOH) and triethylenetetramine were purchased from Shanghai Macklin Biochemical Technology Co., Ltd. All materials were of analytical grade and used as received without further purification. Deionized water made in laboratory was used to prepare all solutions.

2.2. Fabrication of the PEA
The PEA was prepared by dissolving 0.081 g adenine in 1.7 g DMSO, followed with 1 g PEGDE and 0.049 g triethylenetetramine were added. A uniform transparent solution was obtained by stirring, then cured at 100 °C and aged at 140 °C for 6 h to form a gel. The gel was soaked in deionized water for 7 days at atmospheric temperature, and the deionized water was replaced in time to remove the dissolved and unreacted components. Finally, the PEA was obtained by freeze-drying method (figure 1).

2.3. Characterization and testing
Scanning electron microscope (SEM, ZEISS sigma500) and specific surface area and pore size analysis (BET, Micromeritics ASAP2020) were choose to observe the morphology and microstructure, pore structure and specific surface area, respectively. In order to confirm the structure of PEA and the success of ring-opening polymerization, Fourier transform infrared spectroscopy (FT-IR, Nicolet ISS) test was conducted with KBr particles. Similarly, in order to investigate the morphology of PEA, X-ray diffraction spectrometer (XRD, Panaco X’Pert PRO)
was used. Inductively coupled plasma spectroscopy/mass spectrometry (ICP-AES/MS, Agilent 720) was used to determine the concentration of Cu$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$ in the solution after adsorption.

2.4. Adsorption experiments

A batch of adsorption experiments were carried out systematically to evaluate the adsorption capacity of PEA on Cu$^{2+}$, including different initial pH, temperature, adsorption time and initial concentration. Competitive adsorption among Cu$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and adsorption-desorption test were also accomplished. All the adsorption tests were performed on a digital water bath oscillator and conducted three times in parallel with 10 ml heavy metal solution and 10 mg PEA. The pH of heavy metal solution was adjusted by 0.1 M HCl and 0.1 M NaOH solution. After reaching the adsorption saturation time, the concentration of heavy metal ions was determined after filtration with 0.22 μm nylon membrane. Nitrates or halides of copper, cadmium, cobalt, nickel were used to prepare the initial solution.

The adsorption of monolayer chemisorption on homogeneous surfaces. Hence, in this study, in order to analyze the adsorption isotherms, Langmuir and Freundlich isotherm models are the most widely used. The adsorption isotherms for Cu$^{2+}$ were established by initial concentrations ranging from 25 mg L$^{-1}$ to 470 mg L$^{-1}$ at 25 °C, 30 °C, 35 °C and 40 °C, respectively. The mixtures were kept at a water bath oscillator (300 r min$^{-1}$, 30 °C) for 24 h to ensure that the adsorption process is saturated. The adsorption experiments were carried out systematically to evaluate the adsorption capacity of PEA on Cu$^{2+}$, including different initial pH, temperature, adsorption time and initial concentration. Competitive adsorption among Cu$^{2+}$, Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$ and adsorption-desorption test were also accomplished. All the adsorption tests were performed on a digital water bath oscillator and conducted three times in parallel with 10 ml heavy metal solution and 10 mg PEA. The pH of heavy metal solution was adjusted by 0.1 M HCl and 0.1 M NaOH solution. After reaching the adsorption saturation time, the concentration of heavy metal ions was determined after filtration with 0.22 μm nylon membrane. Nitrates or halides of copper, cadmium, cobalt, nickel were used to prepare the initial solution.

The calculation formula of adsorption capacity ($q_e$, mg g$^{-1}$) is as follows:

$$q_e = \frac{(C_0 - C_e)}{m}V$$

where $C_0$ and $C_e$ are the initial and final concentration of Cu$^{2+}$ (mg L$^{-1}$), respectively. $V$ is the volume (L) of the Cu$^{2+}$ solution, and $m$ is the weight (g) of the adsorbent.

In the study of initial pH effect, 0.1 M HCl and 0.1 M NaOH solution were used to adjust the pH of the Cu$^{2+}$ solution to the required value in the range of 2 to 6, then 10 mg PEA was added into the sample bottle with 10 ml 240 mg L$^{-1}$ Cu$^{2+}$ solution. The mixtures were kept at a water bath oscillator (300 r min$^{-1}$, 30 °C) for 24 h to ensure that the adsorption process is saturated.

The adsorption kinetics were carried out with the initial concentration of 150 mg L$^{-1}$ at 25 °C. After adding 10 mg PEA, samples were taken out at intervals and tested until the time reaches 420 min. The pseudo-first-order, pseudo-second-order and webber-morris intra-particle diffusion adsorption kinetics models were used to describe the Cu$^{2+}$ adsorption kinetic using the following equations (2)–(4), respectively:

$$\ln (q_e - q_t) = \ln q_e - k_1t$$

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$

$$q_t = k_3t^{1/2} + c$$

among them, $k_1$, $k_2$ and $k_3$ are the pseudo-first-order, pseudo-second-order and internal diffusion rate constant respectively, while $q_t$ and $q_e$ (mg g$^{-1}$) are the adsorption amount of the PEA at time $t$ and equilibrium time, respectively.

The adsorption isotherms for Cu$^{2+}$ solution were established by initial concentrations ranging from 25 mg L$^{-1}$ to 470 mg L$^{-1}$ at 25 °C, 30 °C, 35 °C and 40 °C, respectively. The mixtures were also kept at a water bath oscillator (300 r min$^{-1}$) with corresponding temperature for 24 h to ensure that the adsorption is saturated. Among the adsorption isotherm models, Langmuir and Freundlich models are the most widely used. The Freundlich model is suitable for the adsorption of uneven surfaces, while the Langmuir model is suitable for the adsorption of monolayer chemisorption on homogeneous surfaces. Hence, in this study, in order to analyze the adsorption form energy of PEA and explore its adsorption mechanism, Langmuir isotherm and Freundlich isotherm models were used to investigate the adsorption isotherms. They are expressed as the following equations (5) and (6):

$$\frac{C_e}{q_e} = \frac{C_{e\text{max}}}{q_{\text{max}}} + \frac{1}{q_{\text{max}}b}$$

$$\ln q_e = \ln K_F + \frac{\ln C_e}{n}$$

among them, $q_e$ and $q_{\text{max}}$ (mg g$^{-1}$) are the equilibrium and maximum adsorption capacity of PEA, respectively. $C_e$ (mg L$^{-1}$) is the equilibrium concentration of Cu$^{2+}$, and $b$ (L mg$^{-1}$) is the Langmuir adsorption constant related to the free energy of adsorption. $K_F$ (mg g$^{-1}$) is related to the affinity of the adsorbent to the adsorbate and $n$ is a constant.

The adsorption thermodynamics calculation of Cu$^{2+}$ adsorption experiment was investigated and the three thermodynamic parameters, free energy change ($\Delta G$), enthalpy change ($\Delta H$) and entropy change ($\Delta S$) were determined as following equations (7) and (8):

$$\Delta G = -RT \ln K_F^0$$

(7)
where $K_e^0$ is the thermodynamic equilibrium constant, $T$ (K) is the adsorption temperature, and $R$ (8.314 J mol$^{-1}$ K$^{-1}$) is the gas constant.

In competitive adsorption, four heavy metal solutions of the same concentration were used. The mixed solutions of heavy metal solution and PEA were kept at a water bath oscillator (300 r min$^{-1}$, 40 °C) for 24 h before testing. For the adsorption-desorption test, the copper ions loaded PEA was soaked in 0.1 M HCl solution to desorb metal ions and washed several times with deionized water, after that, the PEA was dried to constant weight in 60 °C oven under normal pressure and stored in a dryer for repeated adsorption experiments.

3. Results and discussion

3.1. Characterization of PEA

The prepared PEA was characterized by FT-IR, SEM, XRD and BET, and the obtained results are shown in figures 2 and 3. As shown in figure 2(a), SEM results proved that PEA has obviously macroporous structure and multistage fold, which is beneficial to increase the adsorption capacity. According to the results of the BET test (figures 2(b), (c)), the PEA has Langmuir surface area of 1.41 m$^2$ g$^{-1}$ and adsorption average pore diameter of 55.61 nm, which is consistent with the SEM. It also indicates that the adsorption of copper ion by PEA is not the interception effect of pore, but the surface adsorption effect. The surface adsorption rather than the external diffusion and internal diffusion is the limiting step during the adsorption process.

In the FT-IR spectrum (figure 3(a)), the PEA shows a broad peak near 3395 cm$^{-1}$, which is a stretching vibration of $-\text{OH}$ while shown at 2867.21 cm$^{-1}$ is the stretching vibration of $-\text{CH}_2$ and $-\text{CH}_-$. The peak at 1639.94 cm$^{-1}$ is assigned to the skeleton vibrations of the aromatic ring, which proves that the existence of adenine and the ring-opening polymerization of epoxy with adenine was carried out smoothly. The adsorption peak at 1453.65 cm$^{-1}$ is ascribed to the bend vibration of $-\text{CH}_2$ and $-\text{CH}_-$ while the peaks at 1348.60–1248.13 cm$^{-1}$ are belong to the stretching vibration of C–O and C–N. The characteristic absorption peak of ether, which is the end groups from the raw material of PEGDE, is displayed at 1090.02 cm$^{-1}$. The crystal structure of adsorbent, which can be determined by XRD test, determines the arrangement of their atoms, and affects its chemical activity and absorption properties. According to the XRD spectrum (figure 3(b)), PEA shows
only one broad diffraction signals, which appear near 22°, clearly suggesting the amorphous properties, this is beneficial to increase the contact areas with metal ions.

3.2. Adsorption experiments

3.2.1. The effect of pH

The adsorption sites of adsorbents are the main contributors to the adsorption performance. The different pH values will affect the contact opportunities between hydrogen ions or heavy metal ions with the adsorption sites in the adsorbents. Therefore, the pH value of the heavy metal ion solution will significantly affect the adsorption performance of the adsorbents for heavy metal ions [20].

As shown in figure 4, when the pH value is 2, the concentration of hydrogen ions in the solution is high. This leads to the contact probability of hydrogen ions with the adsorption site of PEA is far greater than that of copper ions, so the adsorption capacity of PEA on copper ions is only 7.1 mg g⁻¹. With the increase of pH, the adsorption capacity increased significantly at pH = 3, as the decrease of hydrogen ion concentration improved the contact opportunity between copper ion with adsorption site. The maximum adsorption capacity of 51.4 mg g⁻¹ was reached when pH=5. However, with the further increase of pH, copper ions will form metal complexes,
resulting in the decrease of PEA adsorption capacity. Based on the above analysis, the pH value corresponding to the maximum adsorption capacity was selected for subsequent experiments.

3.2.2. The adsorption kinetics

The adsorption kinetics was investigated and the main influencing factors of the adsorption rate and the speed-limiting steps were also discussed. As we all know, the adsorption process can be divided into three steps: external diffusion, internal diffusion and surface adsorption. The slowest stage determines the total rate of adsorption. The relevant parameters of adsorption kinetics are important indicators of the adsorption process and cannot be ignored in the design of adsorption process. Currently, pseudo-first-order kinetic model (PFO), pseudo-second-order kinetic model (PSO) and intra-particle diffusion model (IPD) are most used in the adsorption of Cu\(^{2+}\). The PFO is based on the assumption that external diffusion and internal diffusion are the limiting factors of the whole adsorption process, while the PSO model assumes that the chemical interaction between the adsorbent surface and the adsorbate is the limiting stage of the adsorption process and the assumption of IPD is that the diffusion process of adsorbate in the internal pore of adsorbent is the limiting stage. By comparing the fitting results of different equations, an appropriate model was chosen, as preliminary judgment of the adsorption mechanism.

The parameters and plots of the adsorption kinetics results were shown in Table 1 and Figure 5, respectively. As shown in Figure 5(a), the adsorption rate of the gel increased significantly in the first 60 min, and the adsorption capacity reached 44.2 mg g\(^{-1}\) at 180 min. In this stage, the adsorption site of PEA is not fully saturated, and gradually saturated with the passage of adsorption time [21]. The PFO, PSO and IPD kinetic model plots are shown in Figures 5(b)–(d), respectively. The R\(^2\) value of PSO is 0.9993, which is higher than PFO and IPD, with the values are 0.6270 and 0.5152, respectively. The saturation adsorption capacity calculated by PSO simulation is in good agreement with the experimental data. Therefore, the PSO model was considered to be the best fitting model with the experimental kinetic data, which indicates that the chemisorption was the limiting step in the adsorption of Cu\(^{2+}\) by PEA, according to the assumption of PSO model.
3.2.3. The adsorption isotherms

The adsorption isotherms experiments were also investigated, which included the effect of different initial concentrations of Cu\(^{2+}\) on the adsorption at different temperatures. The adsorption isotherms and the Freundlich, Langmuir model related parameters for the adsorption of Cu\(^{2+}\) on PEA are shown in the figure 6 and table 2, respectively. As shown in figure 6(a), in the process of increasing the temperature from 25 °C to 40 °C, the maximum adsorption capacity of PEA increased, which indicates that the Cu\(^{2+}\) adsorption is an endothermic process. Increasing the temperature will improve the thermal activity of the adsorption sites on the PEA surface to promote the adsorption and improve the adsorption capacity of the pores [22].

By comparing the correlation coefficients (R\(^2\)) in table 1, it can be concluded that the Langmuir model is more suitable for description of adsorption than Freundlich model, which is consistent with figures 6(b) and (c). The maximum adsorption capacity of PEA towards Cu\(^{2+}\) is 80.1 mg g\(^{-1}\) at 40 °C according to Langmuir model.

According to the applicable conditions of the two models and the simulation results, the adsorption process of PEA on copper ion is surface chemisorption.

3.2.4. Adsorption thermodynamics

The adsorption thermodynamics experiments were carried out to investigate the extent and driving force of the adsorption process and try to explain various factors on adsorption. In particular, the three basic thermodynamic parameters, which are free energy change (\(\Delta G\)), enthalpy change (\(\Delta H\)) and entropy change (\(\Delta S\)), were used to evaluate the thermodynamic feasibility [23]. The value of free energy change (\(\Delta G\)) at different temperatures can be obtained by using the adsorption isotherm at different temperatures, enthalpy change (\(\Delta H\)) and entropy change (\(\Delta S\)) can be determined from the plot of ln K\(_0\) to 1/T [24], according to equations (7) and (8). In solid-liquid adsorption, the heat of adsorption is the enthalpy change, which is the comprehensive result of the energy change during the adsorption process, and can distinguish chemical adsorption and physical adsorption.

The values of \(\Delta G\) at different temperature are shown in table 3, while the values of \(\Delta H\) and \(\Delta S\) are 29.10 kJ mol\(^{-1}\) and 0.083 kJ mol\(^{-1}\) K\(^{-1}\), respectively. The negative value of \(\Delta G\) decreases with increasing temperature, indicating that adsorption was a spontaneous process. The enthalpy value (\(\Delta H\)) was calculated to be 29.10 kJ mol\(^{-1}\), which was positive, indicating that the adsorption was an endothermic process, which is consistent with the results of adsorption isotherm. Higher temperature would more conducive to adsorption as the improvement of the thermal activity of the PEA surface. As the exothermic adsorption process is usually physical adsorption or chemical adsorption, while the endothermic process is chemical adsorption. For this reason, the positive value of \(\Delta H\) further confirms that the adsorption of Cu\(^{2+}\) is chemical adsorption, rather than physical adsorption. The value of \(\Delta S\) is calculated to be 0.083 kJ mol\(^{-1}\) K\(^{-1}\), which was a positive value indicating that the prepared gel had a good affinity for Cu\(^{2+}\).

3.2.5. Cyclic adsorption

Reusability is important to reduce the whole cost of PEA in practical application. The reusability experiments were performed with 200 mg L\(^{-1}\) Cu\(^{2+}\) solution at 40 °C. The adsorbed PEA was eluted by dilute hydrochloric acid.
acid solution, dried in oven at atmospheric pressure and then repeatedly used in adsorption of copper ion, and the results are shown in figure 7(a). Although the adsorption capacity of PEA for copper ion decreased with the increase of repeated experiments, it still maintained 82% of the first adsorption capacity. This is mainly because acid pickling can remove copper ions from PEA by destroying the direct interaction between copper ions and PEA, making the adsorption site in PEA become vacant site again [25]. The reusability and simple preparation method of PEA make it a practical adsorbent in heavy metal wastewater treatment.

3.2.6. Selective adsorption
The selective adsorption experiments were also investigated to make sure that whether the PEA has higher adsorption capacity towards Cu$^{2+}$ than other heavy metal ions. A solution containing 200 mg L$^{-1}$ of Co$^{2+}$, Ni$^{2+}$, Cu$^{2+}$ and Cd$^{2+}$ was configured, and the results after 24 h adsorption are shown in the figure 7(b). In the mixed solution, the PEA adsorption capacity of Cu$^{2+}$ reached 45.2 mg g$^{-1}$, while the adsorption capacity of Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$ were 14.1 mg g$^{-1}$, 16.7 mg g$^{-1}$ and 16.9 mg g$^{-1}$, respectively. It shows the selective adsorption effect of PEA on Cu$^{2+}$. This phenomenon may be explained by the synergy between electronegativity and effective ion radius of the four ions. As the effective ionic radius of Cu$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ are 57, 55 and 54 pm, Cd$^{2+}$ has the largest effective ionic radius (95 pm) among these four ions [26], indicating that the interaction force between PEA and Cd$^{2+}$ is the weakest, which is corresponding to the lowest adsorption capacity of Cd$^{2+}$ compared with the other three. Cu$^{2+}$, Ni$^{2+}$ and Co$^{2+}$ have similar effective ionic radius and the electronegativity magnitude of these three ions is Ni$^{2+} >$ Cu$^{2+} >$ Co$^{2+}$ as the electronegativity magnitude of Ni, Cu and Co is Ni < Cu < Co [27]. However, due to the synergistic effect of electronegativity and effective ion radius, the binding effect of PEA and Cu$^{2+}$ is stronger than that of Ni$^{2+}$ and Co$^{2+}$ [28].

4. Conclusion
In summary, a porous material was prepared by the ring opening polymerization of PEGDE with adenine by simple sol-gel method. The structure and composition of the PEA were characterized by SEM, FTIR, BET and XRD. The adsorption experiments of copper ion by PEA at different pH, temperature, contact time and initial concentration were studied. The results show that the PEA is macroporous, the optimum pH is 5 and the saturated adsorption time is 180 min. The adsorption kinetics experiment is best fit with the pseudo-second-order kinetic model well, while adsorption isotherms prefer to Langmuir model than Freundlich model and the adsorption thermodynamics indicate that the adsorption process is endothermic and spontaneous. The maximum equilibrium adsorption capacity of copper ion is 80.1 mg g$^{-1}$ at 40 $^\circ$C according to the Langmuir model. The competitive adsorption test shows that PEA has good adsorption capacity of Cu$^{2+}$ reaching 45.2 mg g$^{-1}$, while the adsorption capacity of Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$ are 14.1 mg g$^{-1}$, 16.7 mg g$^{-1}$ and 16.9 mg g$^{-1}$, respectively. The results of repeated adsorption experiments showed that PEA could still adsorb 82% of the first adsorption capacity towards copper ion after 5 times cycle. These results indicate that the PEA can be used as a practical adsorbent for copper ion in sewage disposal.

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Data availability statement
All data that support the findings of this study are included within the article (and any supplementary files).

Declaration of competing interest
The authors declare that they have no competing, personal and financial interests in this manuscript.

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