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A high-performance 3D phosphorus-doped graphene oxide adsorbent for imipramine wastewater treatment

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The presence of pharmaceutical wastes in the environment has adversely impacted the marine biodiversity due to their hazardous and bioaccumulation nature. This research focused on the development of an effective phosphorus-doped 3D graphene oxide with bentonite and carboxymethyl cellulose crosslinking (PG/BCC) for the removal of imipramine in wastewater. The impacts of single factor (adsorbent dosage, initial imipramine concentration, system temperature and contact time) on imipramine adsorption were examined by batch experiments while the interactive impacts of multiple factors and process optimisation were investigated by central composite design (CCD). The greatest adsorption capacity evaluated was 458.95 mg/g at the following CCD optimised operating parameters: 10 mg PG/BCC, 250 ppm initial concentration, 34 min contact time and 321 K temperature. The Langmuir model described well the equilibrium of imipramine adsorption whilst the pseudo-second-order model correlated closely to the kinetic data. The imipramine-PG/BCC system was spontaneous (-19.24 to -27.58 kJ/mol) and endothermic (1.23 to 14.56 kJ/mol) as evaluated from thermodynamic modelling. Characterisation of PG/BCC by various microscopy and spectroscopy analyses has validated the incorporation of imipramine into PG/BCC adsorbent. Regeneration of used PG/BCC was proven to be highly feasible with methanol eluent. Conclusively, the findings strongly advocate PG/BCC as a highly feasible and sustainable graphene-based adsorbent for imipramine separation from pharmaceutical wastewater.

1. Introduction

The utilisation of medicinal products has escalated in recent years, particularly during the outbreak of coronavirus disease 2019 (COVID-19) which caused significant loss of human life and tremendous pressure on the mental health of patients. Although the global pandemic accelerated the growth of the pharmaceutical market, it also led to increased environmental pollution with the generation of considerable amounts of pharmaceutical waste. Besides polluting the environment, exposure to active pharmaceutical waste can give rise to negative health impacts. Imipramine is one of the most common tricyclic antidepressants (TCAs) widely applied to treat depression, panic disorder and anxiety. The consumption of TCAs was found to increase by approximately 10% annually while their prescriptions, sales and prices have increased since the start of the COVID-19 pandemic. The increasing usage of TCAs has resulted in traceable amounts of imipramine being detected in the aquatic environment indicating the low efficiency of existing remediation methods. Due to the high bioaccumulation capability and toxicity at concentrations greater than 500 ng/mL, it is necessary to remove TCAs such as imipramine from water sources.

Treatment technologies such as photodegradation, biological treatment, liquid extraction and adsorption have been employed to remediate imipramine-laden wastewater. Among these technologies, adsorption is a comparatively straightforward process with prospective applications in pharmaceutical removal. Generally, adsorption is a cost-effective and sustainable separation system considering its relatively low energy requirement and long operational life when combined with adsorbent regeneration. Numerous investigations on pollutants adsorption using graphene oxide (GO) have recommended this nano-sized adsorbent (nanosorbent) as a strong candidate for wastewater treatment applications involving pollutants...
such as heavy metals [13,14], dyes [15,16] and pharmaceutical residues [17–19]. The ultra-high surface area, bountiful oxygenated chemical functional groups and large ratio of modification aspect render GO as a valuable adsorbing nanomaterial [14]. Nevertheless, the high water dispersibility of GO makes its separation from the aqueous media very challenging and costly after adsorption. Moreover, the agglomeration of GO can decrease its effective surface area leading to lower adsorption efficiency [20]. To resolve the impracticalities of this nanosorbent, crosslinking individual GO sheets into a three-dimensional (3D) structure is desirable for improving the GO recovery and contact area with aqueous pollutants.

A 3D GO configuration in the form of aerogel, hydrogel, foam or monolith can facilitate bulk synthesis without altering the intrinsic properties of the nanomaterial. At the same time, this approach can reinforce the adsorption efficiency of the nanomaterial [21]. As an example, a 3D peanut shell-supported GO aerogel synthesised for non-floxacin adsorption demonstrated an outstanding adsorption capacity of 228.83 mg/g [22]. In a separate study, a 3D GO foam embodied with melthyldiaminium–amide liquid portrayed 501.3 mg/g adsorption capacity for direct red 80 dye, while attaining 99% efficiency after four cycles of adsorption–desorption [23]. A 3D graphene adsorbent demonstrated superior performance for methylene blue dye removal with 221.77 mg/g adsorption capacity which was 50% higher than that of a two-dimensional (2D) GO [24]. The reported findings firmly validated the 3D GO structure applicability in pharmaceutical wastewater treatment. Moreover, environmental issues were minimised with the ease of retrieving the 3D GO from aqueous media and regenerating the adsorbent.

The transformation of the 2D GO sheets into 3D GO based adsorbents can be performed via ice-templating which is a versatile technique for shaping porous materials [25]. In this method, matter is segregated via solution crystallisation and the crystals formed are sublimated under certain conditions, followed by densification of solid through sintering. Freeze drying of the solution entraps the GO nanosheets between neighbouring ice crystals which forms a 3D GO configuration upon sublimation [26]. To stabilise and fortify the 3D structure, incorporation of a crosslinking agent is desirable. Specifically, a chemical additive enables the alteration of suspension viscosity, freezing point, ice expansion effect and microstructure of the 3D GO. Furthermore, the additive promotes the gelation effect of the solvent, thus strengthening the 3D structure of the GO [25].

Carboxymethyl cellulose (CC) is a non-toxic, biocompatible and biodegradable chemical additive that has gained much research interest recently. CC is an anionic and water-soluble cellulose derivative which can be extracted from wood. It contains abundant hydrogen bonded clusters that can enhance crosslinking in the 3D GO structure [27]. In addition, montmorillonite clay, viz. bentonite, can be applied to further strengthen the adsorbent structure. Bentonite which is readily available and non-toxic, has a gibbsite structure sandwiched between two silicon layers, thus forming a strong structural unit with large surface area. Numerous hydroxyl groups are present on its aluminosilicate surface which can facilitate hydrogen bonding. Its crystal layers exhibit negative charges and exchangeable inorganic cations which can be effective in adsorbing cationic compounds [28].

The adsorption performance of the 3D GO structure can be further enhanced by introducing heteroatoms during the GO modification. It has been reported that embedding GO with heteroatoms such as phosphorus, nitrogen and sulphur can stimulate electron transfer between the carbon and heteroatom, a phenomenon which may benefit the adsorption process. For instance, a nitrogen-doped graphene aerogel possessed excellent hydrophobicity with an ultra-light density of 7.19 mg/cm³ and a large adsorption capacity of 206.38 mg/g for pump oil [29]. Based on another study by Feng et al. [30], a boron-nitrogen doped graphene aerogel portrayed adsorption capacities ranging within 100–230 mg/g for organic solvents such as toluene, chloroform, acetonitrile and cyclohexane. In doping GO, phosphorus can form relatively strong bonds between the nanosheet layers. Moreover, the smaller electronegativity and greater size of phosphorus atom compared to carbon atom can result in charge density enlargement and structural distortion, new features that can elevate the adsorption efficiency of GO [30,31].

This research aimed to develop a state-of-the-art 3D hierarchical GO doped with phosphorus and fortified with bentonite and CC (PG/BCC) for the adsorption of imipramine from pharmaceutical wastewater. The PG/BCC adsorbent developed via template-assisted freeze drying method, was utilised for the first time to remove imipramine in aqueous medium. The incorporation of CC to support the 3D GO skeleton offers various advantages such as reinforcement of 3D GO structural stability in aqueous phase, facile separation of adsorbent from treated water at post-adsorption stage and enhancement of regeneration efficiency. Furthermore, GO doped by phosphorus enables tuning of the GO surface charge which may assist in imipramine attachment. To the best knowledge of the author, this is the first paper demonstrating the adsorption performance of PG/BCC in removing imipramine through experimental and mathematical modelling studies, along with regeneration for recycling usage. Different parameters of imipramine adsorption were investigated to establish suitable operating conditions for highest removal of imipramine. The adsorption and regeneration potentials of PG/BCC were also examined by regressing the experimental data to theoretical adsorption models. Simultaneous interactions of multiple parameters on imipramine adsorption and process optimisation were studied by response surface methodology using central composite design (CCD). CCD has been proven to accurately predict the interactive influences of adsorption parameters and provide the optimum parameters for the best adsorption performance [32].

2. Materials and methods

2.1. Materials

The research materials procured from Sigma Aldrich, Germany, were graphite flakes (99.9%), bentonite powder (100%), sodium nitrate (NaNO₃, 99.5%), potassium permanganate (KMN₄, 99%), potassium nitrate (KNO₃, 99%) and imipramine hydrochloride (C₂₅H₂₃ClN₂, 98%, 280.407 g/mol); from R&M, Malaysia, were carboxymethyl cellulose (CC, 99.5%) and methanol (CH₃OH, 99.8%), and from Fischer Scientific, USA, were hydrochloric acid (HCl, 37%), sodium hydroxide (NaOH, 99%), potassium nitrate (KNO₃, 99%), sulphuric acid (H₂SO₄, 95%), hydrogen peroxide (H₂O₂, 30%) and phosphoric acid (H₃PO₄, 85%). These materials were utilised in their received forms, without additional treatment steps being applied.

2.2. Synthesis of adsorbent

The main starting material for the adsorbent preparation was graphene oxide (GO) synthesised by the modified Hummers technique [16]. The construction of 3D GO-based adsorbent begun by contacting 0.2 g GO with 100 mL phosphoric solution (15 mol/L) at 363 K, for 12 h. The resultant suspension was rinsed and dried to form the intermediate product of phosphorus-doped GO (PGO). 0.1 g PGO was sonicated for 15 min in 50 mL of ultrapure (UP) water. Thereafter, 0.7 g of bentonite was added and sonicated for another 30 min. 0.7 g of CC was then poured into the mixture under continuous agitation for 24 h. After that, it was transferred into a mould and frozen at 253 K for 8 h. The sample was freeze dried at 218 K, for overnight and then carbonised at 473 K to produce the PG/BCC adsorbent.

2.3. Characterisation study

The morphological properties of the as-synthesised adsorbent were determined by transmission electron microscopy (TEM, JEOL 2100F, USA) and field emission scanning electron microscopy (FESEM, FEI Quanta 400F, USA). Meanwhile, the thermal stability of PG/BCC was
evaluated by a thermogravimetric analyser (TGA, Mettler Toledo, USA). In this analysis, the adsorbent was exposed to nitrogen gas (50 mL/min) heated from 303 to 1073 K at 10 K/min ramping rate. Upon reaching 1073 K, it was contacted with oxygen gas (50 mL/min) for 15 min. Thereafter, the sample was heated to 1223 K and maintained at this condition for 15 min. In an energy dispersive X-ray (EDX, Oxford Instruments INCA 400, UK), the elemental composition of PG/BCC adsorbent was determined, whereby a small amount of the sample was scanned at 20 kV and 2000–5000 magnifications. The chemical functional groups of PG/BCC were identified by a Fourier transform infrared (FTIR, Spectrum RXI Perkin Elmer, USA). The specimen was gently probed at 2 cm⁻¹ spectral resolution and within 400–4000 cm⁻¹ infrared wavelengths. The crystallinity of the samples was investigated by an X-ray diffraction analyser (XRD, PANalytical, USA) using CuKα radiation (λ = 0.15 nm) at 40 kV and 30 mA, and spectrum range of 10° ≤ 2θ ≤ 75°. X-ray photoelectron spectroscopie (XPS, Axis Ultra DLD Kratos/ Shimadzu, Japan) was used to generate data on the binding energy and chemical state of elements within the adsorbent. The point of zero charge (PZC) test was carried out by adding 15 mg of PG/BCC into several conical flasks containing 40 mL of KNO₃ solutions (0.1 mol/L) of varying pH (3–9). The mixtures were then agitated in a waterbath shaker (Protech, Malaysia) at 200 rpm and 303 K, overnight. Finally, the pH reading of the mixtures was recorded.

2.4. Batch study

1000 ppm of imipramine starting medium was made by dissolving imipramine hydrochloride powder in UP water. It was diluted with the required amounts of UP water to make desired concentrations of imipramine solution for the adsorption experiments. In these tests, a known mass of PG/BCC was contacted with 40 mL of imipramine solution of fixed concentration. The mixtures were shaken at 200 rpm in the waterbath. The parameters altered for the adsorption studies included dosage of PG/BCC (5–30 mg), initial concentration of imipramine solution (20–300 ppm), contact time of imipramine and PG/BCC (5–120 min), temperature of solution (303–323 K) and pH of imipramine solution (3–9). After completion of a test, particles-liquid separation was performed using a PTFE membrane of 0.45 μm pore size (Chromafil, Germany). The filtrate was collected in 2 mL vials for imipramine concentration measurement by high performance liquid chromatography (HPLC 1260, Agilent Technologies, USA) at 250 nm detection wavelength. The mobile phase contained 40% of acetonitrile solution (1 mL/min, C₂H₅N₄, HPLC grade, Fischer Scientific, USA). The imipramine removal percentage, R (%), and adsorption capacity, qₑ (mg/g), are expressed by Eqs. (1) and (2), respectively.

\[ R = \left[ 1 - \frac{C_e}{C_o} \right] \times 100\% \]

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

where \( C_o \) (ppm) is the imipramine concentration at equilibrium, \( C_e \) (ppm) is the initial imipramine concentration, \( V \) (L) is the solution volume and \( m \) (g) is the PG/BCC mass.

2.5. Central composite design

In central composite design (CCD) study, the factors were randomised and modified over 5 levels, namely axial points (+2 and −2), factorial points (+1 and −1) and centre point (0) to display the relationship between the pivotal factors. In this study, adsorption capacity was opted as the response for the CCD model. The system parameters were optimised by Derringer’s desirability method to detect the greatest adsorption capacity for imipramine. Table 1 demonstrates the experimental factors with the respective coded levels, whereas Table 2 shows the details of the CCD matrix. The imipramine adsorption onto PG/BCC was mathematically modelled as a polynomial equation based on simultaneous interactions of the experimental factors.

2.6. Regeneration study

The regeneration of PG/BCC adsorbent was carried out in consecutive adsorption–desorption cycles, with the first adsorption run involving shaking 10 mg of the adsorbent and 40 mL of aqueous imipramine (50 ppm) in the waterbath at 303 K for 2 h. Then, desorption of the used adsorbent was performed by contacting it with 10 mL of eluent for an hour. Thereafter, the desorbed PG/BCC adsorbent was thoroughly rinsed with UP water prior to the next adsorption test. Several eluting solutions (HCl, NaOH, CH₃OH) were applied in the preliminary screening test. The findings from this test suggested CH₃OH as the most suitable eluent for PG/BCC adsorbent due to the highest overall regeneration efficiency obtained over the repeated adsorption–desorption cycles. Therefore, subsequent regeneration tests were carried out using CH₃OH solutions and the effect of the eluent concentrations (30%, 70%, 100%) was investigated. The regeneration efficiency was determined by Eq. (3).

![Table 1](image1.png)

![Table 2](image2.png)
Regeneration efficiency(%) = \frac{\text{Total amount of imipramine desorbed (mg)}}{\text{Total amount of imipramine adsorbed (mg)}} \times 100\% \quad (3)

2.7. Adsorption modelling

The adsorption equilibrium data on imipramine uptake by PG/BCC were fitted to the Freundlich, Langmuir and Temkin models, while the kinetic data were correlated to the pseudo-first-order (PFO), pseudo-second-order (PSO) and Elovich models. The intraparticle diffusion model was applied to identify the rate controlling adsorption step. The best-fitting models for the adsorption equilibrium and kinetic performances of PG/BCC were judged by correlation coefficient (R²) and root-mean-square error (RMSE). Table 3 displays the equations used in this study.

2.8. Thermodynamics study

Gibbs free energy, \( \Delta G \) (kJ/mol), enthalpy change, \( \Delta H \) (kJ/mol), and entropy change, \( \Delta S \) (kJ/mol K), were evaluated to determine the thermodynamic attributes of imipramine-PG/BCC adsorption system. The expressions of these parameters are demonstrated by Eqs. (4)–(6).

\[
\Delta G = -RT\ln K_c \quad (4)
\]

\[
\Delta G = \Delta H - T\Delta S \quad (5)
\]

\[
K_c = \frac{q_e}{C_e} \quad (6)
\]

where \( R \) (J/mol K) is the universal gas constant, \( T \) (K) is the absolute temperature and \( K_c \) (L/g) is the equilibrium constant. A graph of \( \Delta G \) against \( T \) was plotted to determine the values of \( \Delta S \) and \( \Delta H \) from the slope and intercept of the graph, respectively.

3. Results and discussion

3.1. Characteristics of adsorbent

3.1.1. Transmission electron and field emission scanning electron microscopies

TEM and FESEM images were acquired to gain insights into the morphological features of GO and PG/BCC adsorbent at nanometer and micrometer scales, respectively. Fig. 1(a) which represents the TEM image of GO, indicates the smooth, transparent and thin layered structure of the nanomaterial, as well as the nano-shaped wrinkles and ripples at the edges of the GO layers. These observations are in-line with the findings of other published works on GO [42,43]. The TEM images of PG/BCC are illustrated in Fig. 1(b) and (c). It was observed that the composite material was amorphous and embedded with solid particulates (Fig. 1(b)) [44], contributed by CC, bentonite and phosphorus during the synthesis of the adsorbent. Additionally, the adsorbent surface contained evenly distributed nano-size openings (Fig. 1(c)) which were surrounded by the layered doped GO [45]. These results indicated the successful incorporation of phosphorus, bentonite and CC into the 3D GO network, which has significantly altered the GO structure. Meanwhile, the FESEM images are shown in Fig. 1(d) and (e) for PG/BCC before and after imipramine adsorption, respectively. The pristine PG/BCC (Fig. 1(d)) contained cavities and voids across its surface, possibly with active sites for the adsorption of imipramine. These open channels could be formed at the freeze drying stage when moisture was sublimated. The porous structure might enhance the adsorbent surface area, hence making it easier for imipramine molecules to access the sorption sites or functional groups located at the adsorbent interior [46]. After imipramine adsorption, the structure of PG/BCC (Fig. 1(e)) remained porous which could be due to its strong 3D graphene framework. Therefore, the uptake of imipramine has not affected the overall 3D structure of PG/BCC. Fig. 1(f) illustrates the elemental mapping of PG/BCC, revealing scattered white spots of phosphorus atoms. This finding highlighted the success in doping the heteroatom into the 3D GO network.

3.1.2. Energy dispersive X-ray

EDX analysis was conducted to establish the elemental composition of PG/BCC. Fig. 2(a) and (b) describe the EDX spectra of the adsorbent before and after imipramine adsorption, respectively. The PG/BCC adsorbent was mainly composed of GO and hence, major peaks of carbon and oxygen were detected at 0.3 and 0.5 keV, respectively (Fig. 2(a)). These findings agreed well with the literature data for carbonaceous materials detected within the energy range of 0.28–0.32 keV, and for oxygen presence at approximately 0.53 keV [26]. The distinct Si peak was due to this element being the main constituent of bentonite. Traces of Mg, Ca, Fe and O from bentonite were also detected. The main elements were not affected significantly following the adsorption of imipramine, and this finding furtherhighlighted the robustness of PG/BCC. The phosphorus content before (0.19 wt%) and after (0.17 wt%) imipramine adsorption remained relatively constant, hence, supporting that the heteroatom has indeed been embedded in the 3D graphene composite. The presence of nitrogen and chlorine in the EDX spectrum after adsorption (Fig. 2(b)) signified the uptake of imipramine (C19H23ClN2) by the adsorbent.

3.1.3. Thermoanalytic analysis

Fig. 2(c) denotes the changes in weights of PG/BCC (with bentonite) and PG/CC (without bentonite) as a function of temperature. The first stage of weight changes for PG/BCC (5.44%) and PG/CC (6.48%) occurred at 313–373 K which was due to moisture evaporation from the
samples [47]. The following weight losses of PG/BCC (23.98%) and PG/CC (34.88%) at 373–613 K were ascribed to the devolatilisation of matter. Meanwhile, the third stage of PG/BCC (12.76%) and PG/CC (19.18%) weight reductions occurred at a slower rate within 613–1073 K due to further breakdown of remaining volatile matter. At 1073 K, the introduction of oxygen has led to a sharp weight drop for PG/BCC (6.31%) and PG/CC (16.06%) as fixed carbon was thermally degraded [48]. The percentage weight losses of both samples were relatively constant as the temperature was increased to 1223 K. The TGA results revealed that PG/BCC was composed of moisture (5.44%), volatile matter (36.75%), fixed carbon (6.31%) and ash (51.50%). The relatively high ash content implies the successful incorporation of bentonite within the adsorbent and this finding is consistent with the TGA result for a pure bentonite reported in the literature [49].

In comparison, the overall weight loss of PG/BCC was much lower than that of PG/CC (Fig. 2(c)) indicating that the incorporation of bentonite into the 3D GO had strengthened the thermal stability of the 3D graphene structure, and this feature can be beneficial for practical applications in pharmaceutical wastewater treatment.

3.1.4. Fourier transform infrared

Fig. 3(a) illustrates the FTIR peaks of PG/BCC before and after imipramine adsorption within the wavenumber range of 400–4000 cm\(^{-1}\). The FTIR study reaffirmed the presence of abundant oxygenated functional groups in PG/BCC, favourable for imipramine adsorption. The peaks at 1312, 3254 and 3608 cm\(^{-1}\) were related to stretching vibration of O–H in phenol, carboxylates and hydroxyl groups, respectively [11]. The strong adsorption peak at 463 cm\(^{-1}\) was assigned to C–H bending. Meanwhile, the distinctive peak at 1018 cm\(^{-1}\) was matched to C–O bending in carboxylic acid, 635 cm\(^{-1}\) was due to C–Cl bending in chlorine compound, 1600 cm\(^{-1}\) was linked to sp\(^2\) hybridised C = C stretching and lastly, 2932 cm\(^{-1}\) was due to sp\(^2\) and sp\(^3\) hybridised C–H skeleton networks [50]. Furthermore, the peak at 917 cm\(^{-1}\) was due to P–OH bending/P–O stretching/P–O–P asymmetric stretching vibration while the peak at 1099 cm\(^{-1}\) was ascribed to P–O bond/P–O–P symmetric stretching vibration [51,52]. The C–P stretching bond at 1420 cm\(^{-1}\) signified the occurrence of substiututional doping [52,53].

After imipramine adsorption, some chemical functionalities of the adsorbent were altered, as indicated by an overall reduction of peak intensity (Fig. 3(a)). The absence of peaks at 1312 and 3608 cm\(^{-1}\) together with the shift of peak from 3254 to 3221 cm\(^{-1}\) indicated that O–H stretching vibration was affected by the imipramine adsorption. A distinct transmittance reduction of peak at 1018 cm\(^{-1}\) with a slight shift to 1021 cm\(^{-1}\) was due to the modification of C–O bond in carboxylic acid during adsorption [11]. The findings also confirmed that the oxygenated functional groups dominated the active sites of PG/BCC. On the other hand, negligible changes in the peaks for C–H (463 and 2932 cm\(^{-1}\)), C–Cl (635 cm\(^{-1}\)) and C = C (1600 cm\(^{-1}\)) bending vibrations suggested that the carbon atoms of PG/BCC were not involved in imipramine adsorption. The finding further verifying carboxyl and hydroxyl groups contributed to the adsorption of imipramine through formation of hydrogen bonding between the functional groups and the adsorbate [13]. In addition, the phosphorus related peaks (C–P, P–O, P–O–P, P–OH) after adsorption confirmed the grafting of phosphorus into the graphene framework and the decrease in overall phosphorus peak intensity indicated the favourable uptake of imipramine by the phosphorus-based functional groups [54].

3.1.5. X-ray diffraction

Fig. 3(b) shows the XRD spectra for GO, PG, bentonite, CC and PG/BCC. For GO, a dominant peak was observed at 2\(\theta\) = 12.53° relating to AB stacking order with an interlayer spacing of 0.71 nm [55]. The
relatively large interlayer spacing of GO implied the successful oxidation of graphite via the modified Hummers method. After phosphorus doping of GO (PG), the peak was slightly reduced and shifted to $2\theta = 11.17^\circ$, but the interlayer spacing ($0.79$ nm) remained nearly constant. This result suggested insignificant changes in the amount of oxygen-containing functional groups after the doping process. The partly crystalline character and low crystallinity of CC was evident from the large diffraction peak at $2\theta = 20.41^\circ$ [56]. After the incorporation of bentonite and CC into the phosphorus-doped GO (PG), the resultant PG/BCC adsorbent exhibited the broadest diffraction peak. The disappearance of GO dominant peak and decrease in interlayer spacing revealed that the GO has been reduced and well-intercalated into a 3D structure [57]. Moreover, the PG/BCC diffraction peaks at $2\theta = 19.61^\circ$, $26.49^\circ$, $35.23^\circ$, $49.25^\circ$ and $61.67^\circ$ resembled the characteristic peaks of bentonite and CC as shown in Fig. 3(b), denoting the successful inclusion of bentonite and CC into the PG/BCC adsorbent.

3.1.6. X-ray photoelectron spectroscopy

Fig. 4(a) displays the results of XPS analysis on PG/BCC, where C 1 s spectra of the adsorbent with C–P, C–O and C=O bonds were detected at 285.03, 286.67 and 288.18 eV of binding energies [45,58], respectively. The C–P bond confirmed the successful substitutional doping of phosphorus into the graphene structure which was also confirmed by the FTIR analysis. Fig. 4(b) illustrates the C–O–P (531.34 eV) and C–O (532.71 eV) of O 1 s spectra [52,58]. The weak P 2p intensity (Fig. 4(c)) indicates the P–O (131.75 eV) and P–C (133.76 eV) species. The XPS analysis further revealed that the phosphorus content of the adsorbent was approximately 0.06 atomic %, correlating well with the EDX result.
3.2. Adsorption performance evaluations

3.2.1. Effect of PG/BCC dosage

The dosage of PG/BCC applied for imipramine adsorption governs the economic viability of the new water treatment system. Fig. 5(a) demonstrates the influence of PG/BCC dosage on the removal efficiency of imipramine. The imipramine percentage removal showed an upward trend from 55.63% to 81.66% as the adsorbent dosage was increased from 5 to 10 mg. The steep increase in the removal percentage was due to the increase in surface area and active sites with increasing PG/BCC dosage, thereby enhancing the imipramine adsorption. The percentage removal eventually reached a plateau state at dosages greater than 10 mg which was due to the increase in number of particles per unit volume that gave rise to agglomeration. The effective sorption sites per unit mass of adsorbent and specific surface area were reduced, thus these lowered the removal of imipramine [26]. Meanwhile, the adsorption capacity showed an opposite trend to the percentage removal, decreasing from 222.54 to 60.90 mg/g with increasing PG/BCC dosage. This outcome could be explained by the augmented adsorbent mass at constant imipramine concentration causing the active sites to remain unsaturated [59]. Consequently, 10 mg PG/BCC was selected as the suitable dosage for subsequent adsorption study as it showed comparatively large removal percentage (81.66%) and adsorption capacity (163.31 mg/g) of imipramine.

3.2.2. Effect of pH

Fig. 5(b) illustrates the PZC of PG/BCC occurred at pH 6 indicating that the adsorbent was positively charged at solution pH < 6 and negatively charged at solution pH greater than 6. Meanwhile, the impact of varying solution pH (3–9) on the removal percentage of imipramine is represented by Fig. 5(c). It was observed that the removal percentage (64.02%) was relatively low at pH 3. Under this extremely acidic condition, the adsorbent was positively charged (PZC = pH 6) due to the protonation of functional groups of GO. Thus, the strong electrostatic repulsion between imipramine cations and protonated sites of PG/BCC resulted in the low adsorption activity. Moreover, the low imipramine removal under this acidic condition could be due to competitive adsorption between imipramine cations and protons. There was a sharp increase in removal percentage to 92.90% as the pH was increased from 3 to 4, and removals were maintained at relatively high values (92.90–93.69%) within the pH range of 4 to 9. As the PZC of the PG/BCC adsorbent was 6, the high removal of imipramine between pH 6–9 could be due to electrostatic attraction between the negatively charged adsorbent surface and the imipramine cations, while between pH 4–6 other forms of binding mechanisms such as hydrogen bonding, π-π stacking and hydrophobic interaction might be dominating the removal process [60, 61].

Fig. 5(c) also shows the control test plot, where the removal of imipramine between pH 3–4 and 8–9 (without adsorbent) might be due to changes in the molecular structure of imipramine under the extremely acidic and alkaline environments [24]. Nevertheless, the removal percentage was relatively high between pH 4–9, and the natural pH of imipramine solution was 5. Hence, pH adjustment was not necessary when conducting the batch operation at the natural solution pH. Summarily, the direct use of PG/BCC in treatment of pharmaceutical wastewater and the wide pH range tolerance of the adsorbent are advantageous as no additional chemical is required for pH alteration.

3.3. Adsorption equilibrium

The equilibrium relationship between imipramine and PG/BCC under isothermal condition was studied through regression of the experimental data to the original form of Langmuir, Freundlich and Temkin correlations, as shown in Fig. 6. Table 4 reveals the equilibrium parameters for imipramine adsorption onto PG/BCC. Following comparison between the $R^2$ and RMSE values of the different models (Table 4), it was found that the imipramine adsorption was most appropriately represented by the Langmuir model, exhibiting greatest $R^2$ (0.970–0.985) and smallest RMSE (17.62–30.91). Apart from that, the Langmuir curves in Fig. 6(a)–(c) verified the close fit of the measured data to the model predicted data. This discovery implied that a single layer of imipramine molecules was attached to homogenous sites of PG/BCC without any interactions between neighbouring molecules [62, 63]. The highest Langmuir monolayer adsorption capacity ($q_m$) was estimated at 462.12 mg/g, with an isotherm constant of 0.072 L/mg at 323 K. It can be seen from Table 4 that $q_m$ increases with temperature implying the endothermicity of imipramine adsorption by the adsorbent. Hence, the adsorption process was enhanced with the mobility of imipramine adsorbates at elevated temperatures.

3.4. Adsorption kinetics

Fig. 7(a) compares the measured data with the data determined by the PFO, PSO and Elovitch models at 20, 50 and 100 ppm. The imipramine adsorption was represented by three phases which included rapid
Adsorption, gradual adsorption and equilibrium. High adsorption rates were observed (Fig. 7(a)) during the initial 5 min due to bountiful active sites in the adsorbent available for imipramine attachment [64]. Subsequently, the gradual adsorption between 5 and 30 min was due to the depletion of vacant sorption sites that in turn lowered the rate of adsorption. The equilibrium phase was reached after 30 min of adsorption, indicating that the binding sites were fully saturated. The rapid adsorption equilibrium attained within 30 min suggested that the PG/BCC adsorbent was effective for imipramine removal.

The kinetic study is essential for determining the rate and mechanism of imipramine adsorption. Table 5 lists the kinetic parameters of the models. The largest $R^2$ (0.993–0.997) and smallest RMSE (1.521–5.654) values of the PSO model implied that this kinetic model correlated well to the experimental data. Additionally, the relatively high similarity between the experimental adsorption capacity (47.14–220.36 mg/g) and calculated adsorption capacity (46.39–231.35 mg/g) served as further evidence for the suitability of the PSO model in representing the adsorption kinetic. Hence, the imipramine removal by PG/BCC can be considered as a chemisorption-governed mechanism involving electrons sharing/exchange between imipramine and the adsorbent functional groups. The reduction in the rate constant, $k_2$, with increasing concentration was due to greater driving force at higher imipramine concentrations to overcome the mass transfer resistances thereby allowing the sorption sites to be easily occupied [65].

The intraparticle diffusion model was applied for the identification of rate determining step by plotting the adsorption capacity against the square root of time. Fig. 7(b) presents the intraparticle diffusion plots at different initial concentrations of imipramine. The plots were not linear and did not pass through the origin, and these results suggested that intraparticle diffusion was not the only mechanism restricting the adsorption rate. Other transport mechanisms such as boundary layer could also be involved [66,67].

3.5. Adsorption thermodynamics

The thermodynamic analysis enables determination of the feasibility and spontaneity of imipramine adsorption. The spontaneity of the process was classified by $\Delta G$ value, whereby a negative $\Delta G$ defines the adsorption as spontaneous and vice versa. Table 6 displays the thermodynamic constants for the imipramine-PG/BCC system. The high feasibility and spontaneity of imipramine adsorption were established based on the negative $\Delta G$ values under all temperatures and concentrations assayed. At a fixed concentration, the increase in negativity of $\Delta G$ with increasing temperature confirmed the higher spontaneity and favourability of imipramine adsorption at higher temperatures. The high adsorption capacities at high temperatures could be explained by the
positive $\Delta H$ values (2.358–14.56 kJ/mol) suggesting the process was endothermic. The $\Delta H$ values also implied that the adsorption might have occurred through physical interactions [68]. The negative $\Delta S$ values (-0.084 to -0.118 kJ/mol $\cdot$ K) were due to the decline in randomness at the solid–liquid interface via the adsorption of imipramine.

3.6. Response surface methodology

3.6.1. Model construction

The interactive effects of four factors (Table 1) on imipramine adsorption were evaluated using CCD. The measured responses for the 30 experimental runs are displayed in Table 2. Through modelling of the experimental data by CCD approach, a mathematical model was constructed to signify the relationship between the independent parameters and process response, $q_e$. The predicted response was expressed in un-coded units as shown by Eq. (7).

$$q_e = -260.99 - 10.35A + 2.95B + 45.04C - 19.52D - 0.05AB - 0.43AC + 0.61AD + 0.025BC + 0.0012BD - 0.17CD - 0.0031A^2 - 0.0048B^2 - 0.53C^2 + 0.19D^2$$

The model proved to be a good representation of the adsorption process with residual errors ranging from 0.397% to 23.99%. The magnitude of coefficients indicates the degree of impact of the parameter, while the sign of coefficients shows whether the adsorption was...
positively or negatively impacted. These can be judged from the mathematical model expressed in coded values by Eq. (8):

\[
q_t = 288.17 - 36.25A + 74.70B + 19.27C + 1.25D - 13.64AB - 10.72AC
+ 15.15AD + 6.25BC + 0.29BD - 4.23CD - 0.079C^2 - 11.94B^2
- 13.22C^2 + 4.87D^2
\]

The positive sign of factors B, C and D symbolises a synergistic influence of initial concentration, contact time and temperature on \( q_t \). The negative impact on \( q_t \) by the adsorbent dosage (A) was shown by the negative sign in Eq. (8). Furthermore, factor B contributed a more significant effect on the imipramine removal due to its highest magnitude compared to the other model terms.

### 3.6.2. ANOVA

ANOVA test was performed on the predicted data to validate the statistical significance of the quadratic model. Table 7 compiles the ANOVA results and statistics for the response surface model and the independent parameters. The model appeared to be significant with satisfactorily high F-value (63.61) and a P-value lower than 0.0001, at which the large former value and small value of the latter indicated the great significance of the respective coefficients. In terms of F-value, the probability of such a large number assignable to noise interruption was only 0.01%. Concurrently, the model terms with high intensities were contributed by the P-values smaller than 0.05. As delineated in Table 7, the model terms of A, B, C, AB, AC, AD, B^2 and C^2 were the variables and interactions that caused significant influences on imipramine uptake by PG/BCC as compared to the remaining factor coefficients. Type III Sum of Squares was implemented for ANOVA analysis since this approach specified significant interactive responses between the independent variables [69]. The Type III Sum of Squares is used as the indicator to determine the primary effects of the investigated factors. As shown in Table 7, the highest value of sum of squares of adsorbent dosage (31333.36) and the initial imipramine concentration (1.34E+05) supported that both parameters would give rise to the largest impacts on the imipramine adsorption process. Thereafter, the validity of the expressed quadratic model was recognised by the lack-of-fit evaluation [70]. The model construction was proven by an exact functional correlation between the significant variables and the response as the lack-offit F-value obtained was 0.84, at which the statistically insignificant lack-of-fit F-value implied that the lack-of-fit was relatively negligible as compared to the pure error. The lack-of-fit P-value (0.6203) demonstrated 62.03% of possibility that the small lack-of-fit F-value occurred due to noise.

The \( R^2 \) of the quadratic model was calculated for the determination of degree of model fitting as the closer the \( R^2 \) value was to unity, the greater correlation between the predicted and observed data. An \( R^2 \) value of 0.983 suggested that 98.3% of the total variations on the imipramine adsorption could possibly be linked to the investigated parameters and 1.7% of that was due to the variability of residuals. The small variation in \( R^2 \) (0.983) and adjusted \( R^2 \) (0.968) ensured that only significant model terms were involved for the model construction since \( R^2 \) increased when additional terms were taken into account but the adjusted \( R^2 \) decreased when the inserted factors were low in intensities [71]. Likewise, the data variation examined by the quadratic model was estimated by the adjusted \( R^2 \), whereas the capability of the regressed model in response forecasting was computed using the predicted \( R^2 \). The difference between the adjusted (0.968) and predicted \( R^2 \) (0.931) values was much lower than 0.2 that further supported the good fitting of the model with good agreement between both statistical values. Furthermore, the adequate precision assessed the signal-to-noise ratio through comparison of the predicted response at design points and the average prediction error. A desirable value of adequate precision (34.11) was analysed as being greater than 4, at which the high adequacy of the model response signal allowed high suitability of the model in design...
space navigation. The accuracy of the quadratic model was validated through the application of additional statistical functions, namely standard deviation (std. dev.) and variance (C.V.). A low std. dev. and C.V. < 10% confirmed the high accuracy of the model [72]. As revealed in Table 7, the calculated std. dev. (14.74) was low enough and the C.V. (5.42%) value within 10% further signified the good fitting of the model.

### 3.6.3. Diagnostic and perturbation plots

The diagnostic plots were applied for determining the predictability and adequacy of the quadratic models, while the perturbation plot was

![Diagrams of predicted against actual responses, normal probability against externally studentised residuals, externally studentised residuals against run number, and perturbation for imipramine adsorption onto PG/BCC.](diagram)

**Fig. 8.** Plots of (a) predicted against actual responses; (b) normal probability against externally studentised residuals; (c) externally studentised residuals against run number and (d) perturbation for imipramine adsorption onto PG/BCC.
used for evaluating the relative influence of each factor on the responding adsorption capacity of PG/BCC. Fig. 8(a) illustrates the plot of response predicted by the quadratic model against the actual response. The actual responses which were closely located to the linear predicted response line provided a satisfactory approximation of experimental data to the CCD model. Fig. 8(b) demonstrates the normal distribution of externally studentised residuals for the response of the CCD model. The plot portrays a linear trend with small variations in the deviations indicating the residual errors were normally distributed and the predicted model was in good agreement with the experimental findings [72]. The satisfactory dispersal of residuals in a regular manner with minimal divergences also showed the high degree of fitting of the predicted CCD model to the actual response. Fig. 8(c) defines the performance of outliers for a total of 30 imipramine adsorption experimental runs. The outlier plot enables the identification of probable outliers at abnormal distance from the population of the residuals. The residual is recognised as an outlier when the magnitude lies beyond the general threshold of ± 3% standard deviations. A random distribution of residuals on either side of zero was outlined in Fig. 8(c) with all magnitudes of residual in the range of lower to upper limits. Nearly all of the externally studentised residuals lied within −2 to +2, implying that the model was formulated at a 95% confidence level. Since none of the residuals exceeded ± 3% of the standard deviations, the model had absence of outliers and was efficient in the prediction of interactive effects of parameters.

The perturbation plot, as shown in Fig. 8(d), displays the interactions of the significant parameters on the adsorption capacity of the PG/BCC. Sharp curvatures of A and B were observed from the plot, suggested that

![Fig. 9. 3D response surface plots of imipramine adsorption onto PG/BCC.](image-url)
both variables exhibited higher effects on the process response. Contrarily, the relatively flat lines of C and D represented lower sensitivity of the adsorption capacity to these variables. The outcomes of the perturbation plot synchronised with the findings from ANOVA in Table 7, whereby A and B caused greatest impacts on imipramine adsorption by PG/BCC. Concurrently, the negative trendline of factor A revealed that the increase of adsorbent dosage would affect the imipramine adsorption negatively, and vice versa. Based on the degree of steepness of the curvatures, the response was affected mostly by initial concentration (B), followed by dosage of PG/BCC (A), contact time (C) and temperature (D).

3.6.4. 3D response surface

The simultaneous interactions of the independent parameters and the degree of consequences of relationships between the factors and the adsorption capacity of PG/BCC were assayed by 3D response surface plots. The optimum range of two parameters can be identified when the other two factors are located constantly at the central level of the plots. The four independent factors, namely dosage of PG/BCC (A), initial imipramine concentration (B), contact time (C) and temperature (D) contributing to the quadratic model construction were ranged accordingly in Table 2 for the response surface plotting.

Dosage of PG/BCC (A) served as the second most significant model term in impacting the response as listed in Table 7. Fig. 9(a)–(c) denote the interactions of A with the remaining parameters on the process response, viz. adsorption capacity, $q_e$. Overall, the dosage of PG/BCC was negatively correlated to the imipramine adsorption capacity. The decrease of $q_e$ with increasing dosage was due to the declined ratio of adsorbed amount of imipramine to the amount of adsorbent. Therefore, the active sites of the adsorbent were unsaturated resulting in the decreasing trend. Another reason for the negative impact of dosage on the response was the agglomeration of PG/BCC at high dosage, reducing the effective surface area for imipramine adsorption [71]. Based on the observations from Fig. 9(a)–(c), the possible high $q_e$ was suggested at A $< 15$ mg, B $> 150$ ppm, C $< 30$ min and D $> 313$ K.

Fig. 9(a), (d) and (e) illustrate the interactive influences of B with A, C and D, respectively. Generally, the initial concentration portrayed a dominant synergistic impact on $q_e$ at which high imipramine adsorption capacities (greater than200 mg/g) were obtained when the concentrations in Fig. 9(a), (d) and (e) exceeded 150 ppm. At higher initial concentrations, the greater amount of imipramine molecules as compared to the PG/BCC active sites elevated the driving force to overcome the mass transfer resistance at the solid–liquid interface, thus boosting the adsorption capacity of imipramine [71]. The response surface plots declared that the possible maximum $q_e$ could be achieved when B $> 150$ ppm, A $< 15$ mg, C $< 30$ min and D $> 313$ K.

The interactions of contact time (C) with other parameters and their impacts on the imipramine adsorption is represented by Fig. 9(b), (d) and (f). The overall analysis indicated that $q_e$ had a gradual increase at the initial stage of adsorption (20 $< B < 30$ min) ascribable to the high vacancy of active sites for imipramine uptake within the first 30 min [70]. Beyond 30 min, the increasing trend of adsorption rate was unnoticeable since more binding sites were occupied by the pharmaceutical molecules. A plateau trend was then observed at B greater than 30 min confirming the saturation state of the active sites. The highest possible adsorption capacity of PG/BCC was fulfilled by the conditions of C $< 30$ min, A $< 15$ mg, B $> 150$ ppm and D $> 313$ K.

Fig. 9(c), (e) and (f) display the interactive plots of D with factors A, B and C at the range of 303–322 K. At low temperatures ($< 308$ K), $q_e$ were at relatively low values ($< 400$ mg/g) assignable to the lower rate of collision between imipramine molecules and the binding sites of PG/BCC for the occurrence of adsorption. As the temperature increased, the response $q_e$ increased and this trend supported the thermodynamics findings (Table 6) on the imipramine adsorption process being endothermic, favouring high temperatures for enhanced pharmaceutical attachment [72]. The increasing pattern might be due to the increase in kinetic energy of the adsorbates as temperature was increased, thus giving rise to greater mobility and collision rate between the imipramine molecules and the binding sites of PG/BCC. In this case, the desirable conditions to reach maximum $q_e$ were allocated as D $> 313$ K, A $< 15$ mg, B $> 150$ ppm and C $> 25$ min.

3.6.5. Imipramine adsorption optimisation

Derringer’s desirability function was implemented for the optimisation of process parameters to maximise the adsorption of imipramine onto PG/BCC. The range of each parameter was set prior to determining the optimum model term combination. From the preliminary study, a negative correlation between dosage and adsorption capacity was found and this necessitated the minimisation of adsorbent dosage to achieve an economical removal of imipramine with the maximisation of process response, $q_e$. The remaining parameters were all levelled in range as imipramine concentration and contact time above the maximum limits would not significantly improve the removal efficiency. Additionally, extremely low temperatures lead to low adsorption capacities while very high temperatures would cause physical degradation of the adsorbent. A high desirability (1.0) was attained with the following combination of factors: 10 mg adsorbent dosage, 250 ppm initial concentration, 34 min contact time and 321 K temperature. To further justify the CCD optimised results, triplicate laboratory experiments were performed under these conditions. The predicted results were authenticated with a small deviation (1.28%) between the average $q_e$ (453.08 mg/g) and the predicted $q_e$ (458.95 mg/g) which signified the adequacy of the CCD model.

3.7. Regeneration study

The ability to regenerate exhausted PG/BCC for reuse can assist in cost minimisation besides preventing the formation of secondary solid waste [73]. Fig. 10(a) shows the removal percentage versus regeneration number for 3 different methanol concentrations (30%, 70% and 100%) tested in the desorption study, whereas Fig. 10(b) displays the effects of the eluent concentration and cycle number on regeneration efficiency. As shown in Fig. 10(a), the highest removal efficiencies were achieved for the first two cycles (91.35%–84.45%) when the lowest methanol concentration (30%) was applied for desorption, but the removal efficiencies in the third (50.88%) and fourth (22.80%) cycles were lowest, suggesting this methanol concentration was not favourable for long-term regeneration usage. The results in Fig. 10(b) also indicated that low concentrations of methanol eluent were ineffective in long-term desorption of imipramine from PG/BCC as the regeneration efficiency for the last cycle was only 24.96%. With pure methanol usage, the removal percentages varied from 87.65% to 39.35% (Fig. 10(a)) while moderate regeneration efficiencies of 81.60% to 44.90% were recorded (Fig. 10(b)). The declining trend was observed to be caused by loss of PG/BCC fragments during the experiments. Likewise, partial collapse of the internal 3D PG/BCC structure might also cause the decrease in regeneration efficiency. Therefore, pure methanol was selected as the eluting agent for the PG/BCC adsorbent regeneration owing to its relatively good removal and regeneration efficiencies.

3.8. Adsorption mechanisms

For graphene-based adsorption systems, various adsorption mechanisms could be involved and these include physisorption, chemisorption, π–π stacking, hydrogen bonding, electron-donor–acceptor and hydrophobic interactions [14]. The type of mechanisms occurring in the system are dependent on the nature of adsorbent and adsorbate. For the PG/BCC-imipramine system, the experimental results suggested that the high removal performance was contributed by various mechanisms. From the kinetic study, the PSO provided the best fitting model indicating the occurrence of chemical interactions via electrons sharing between imipramine and the PG/BCC sites, possibly in covalent or ionic...
bonds. On the other hand, physisorption could also occur as indicated by the positive $\Delta H$ values (2.358–14.56 kJ/mol) obtained from the thermodynamic study [68]. Furthermore, the FTIR results proposed the possible occurrence of hydrogen bonding contributed mainly by the carboxyl and hydroxyl groups of PG/BCC [13]. Ultimately, the pH study supported the involvement of multiple adsorption mechanisms including electrostatic interaction and other mechanisms. Hence, the adsorption of imipramine by PG/BCC was not solely based on one mechanism but the synergistic effects of several mechanisms as shown in Fig. 11.

4. Conclusions

In the present study, a new 3D graphene-based adsorbent (PG/BCC) with outstanding adsorption of imipramine was successfully developed via an eco-friendly ice-templating approach. The TEM and FESEM results revealed the surface of PG/BCC contained pores and cavities, and phosphorus which might enhance the adsorption of imipramine. The PG/BCC adsorbent was found to be relative stable within pH 4–9 exhibiting high imipramine adsorption. The adsorption equilibrium and kinetic modelling indicated that monolayer adsorption of imipramine occurred on homogeneous sites and the process was governed by chemisorption. Thermodynamically, the imipramine adsorption was spontaneous and endothermic. The findings from ANOVA and 3D response surface plots suggested initial concentration and PG/BCC dosage as the parameters dominating the adsorption process. Moreover, CCD optimisation yielded a maximum adsorption capacity of 458.95 mg/g at the optimised dosage of 10 mg, initial concentration of 250 ppm, contact time of 34 min and adsorption temperature of 321 K. The regeneration study denoted that pure methanol was a suitable eluent for

Fig. 10. (a) Percentage removal versus regeneration number, and (b) regeneration efficiency versus cycle number at different methanol concentrations.

![Fig. 10](image1)

![Fig. 11](image2)
the regeneration of exhausted PG/BCC with relatively high regeneration efficiency. In essence, PG/BCC is an effective and sustainable 3D graphene-based adsorbent for imipramine removal.

CRediT authorship contribution statement

Wan Ting Tee: Investigation, Methodology, Writing – original draft. Jia En Yong: Investigation, Visualization. Jasmine Chua: Investigation, Data curation. Nicholas Yung Li Loh: Formal analysis, Software. Billie Yan Zhang Hiew: Resources, Validation. Suyin Gan: Validation, Writing – review & editing. Lai Yee Lee: Conceptualization, Funding acquisition, Supervision, Project administration, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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