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# Kinetic modelling and equilibrium behaviour of methylene blue adsorption in sequentially modified PVDF/NC/TiO<sub>2</sub>/carbon based hybrid membranes

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Hybrid polymeric membranes are often evaluated in terms of flux, rejection, and antifouling performance, whereas their adsorption kinetics and equilibrium behaviour are commonly treated as secondary considerations. This separation limits mechanistic understanding because dye removal by functional membranes is governed by the coupling between convective transport, pore-mediated retention, surface adsorption, filler dispersion and foulant–membrane interaction. This study aims to evaluate the kinetic and equilibrium behaviour of methylene blue (MB) adsorption by sequentially modified polyvinylidene fluoride (PVDF)-based hybrid membranes incorporating nanocellulose (NC), titanium dioxide (TiO<sub>2</sub>), graphene (GR) and graphene oxide-derived modified hybrid material (GO-mHM). Correspondingly, this study evaluates adsorption behaviour across the full sequence of membrane modification, enabling a comparative assessment of the contribution of each material component to adsorption kinetics and equilibrium performance, rather than limiting the analysis to the final optimised membrane formulation. Adsorption experiments were conducted at 25 °C using MB concentrations of 1–5 ppm, with adsorption capacity normalised to membrane area. The pseudo second order (PSO) model provided the most consistent kinetic fit with  $R^2$  values generally ranging from 0.96 to 0.98. At 5 ppm MB, the equilibrium adsorption capacity increased from 1049.79 mg m<sup>-2</sup> for pristine PVDF to 2080.69 mg m<sup>-2</sup> for PVDF–4% NCM, followed by further improvement to 2408.14, 2442.68, and 2462.38 mg m<sup>-2</sup> for PVDF/NC/3.0% TiO<sub>2</sub>, PVDF/NC/TiO<sub>2</sub>/0.2% GR, and PVDF/NC/TiO<sub>2</sub>/0.3% GO-mHM, respectively. Isotherm equilibrium modelling showed that the Freundlich model best described MB adsorption which indicates adsorption on a heterogeneous membrane surface with non-uniform adsorption sites. PVDF/NC/TiO<sub>2</sub>/0.3% GO-mHM exhibited the strongest adsorption response, recording a Freundlich  $K_F$  of 75 501.71 mg m<sup>-2</sup>. These findings are consistent with MB adsorption occurring across chemically and structurally heterogeneous membrane domains, with filler composition, dispersion and interfacial accessibility influencing the observed adsorption response. The specific contributions of individual molecular interactions were not directly resolved and are therefore interpreted mechanistically rather than assigned as definitive adsorption pathways.

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## 1 Introduction

Textile dyeing and finishing are increasingly recognised as chemically intensive wet-processing operations that generate highly coloured wastewater containing synthetic dyes, salts, auxiliary chemicals and persistent organic residues. The scale of this issue is reflected in the fashion and textile sectors' reported annual water consumption of approximately 215 trillion litres

and the use of about 15 000 chemicals in textile manufacturing, alongside growing expectations for standardised wastewater and sludge monitoring.<sup>1,2</sup> Methylene blue (MB), a cationic aromatic dye, is widely used as a representative model pollutant for evaluating adsorptive, photocatalytic and membrane-based dye-removal systems. Its persistence in aqueous environments makes it suitable for assessing membrane functionality beyond simple hydraulic performance, particularly where adsorption, surface interaction and solute retention occur simultaneously.<sup>3</sup> Polyvinylidene fluoride (PVDF) is extensively used in membrane fabrication because of its chemical stability, thermal resistance, mechanical robustness and compatibility with phase-inversion processing.<sup>4</sup> Nevertheless, pristine PVDF usually exhibits limited dye-affinity and antifouling performance because of its hydrophobic surface and low density of active polar groups.<sup>5</sup>

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These limitations can reduce water permeability, promote foulant accumulation and restrict effective interaction between dye molecules and the membrane surface. Functional modification of PVDF using hydrophilic, inorganic nanoparticles,<sup>6–8</sup> and carbon-based nanofillers has become an important route for improving membrane hydrophilicity, surface activity, pore architecture and long-term separation stability.<sup>9–11</sup> For adsorptive hybrid membranes, dye removal cannot be interpreted solely as molecular sieving.<sup>12,13</sup> Water flux reflects hydraulic transport through the membrane, whereas dye rejection indicates the ability of the membrane to restrict solute passage. Adsorption kinetic and equilibrium parameters provide additional information on dye interaction with accessible surface domains, accessible pore sites and filler-derived functional groups. Therefore, the interpretation of hybrid membrane performance requires an integrated assessment of permeability, rejection, fouling behaviour and adsorption response. This is particularly important because dye retention may arise from reversible surface adsorption, pore-assisted solute delay, irreversible fouling or reduced solute transport within a modified pore network.

Recent studies in the published literature demonstrate that Fe-based frameworks and TiO<sub>2</sub>–carbon hybrids could enhance hazardous dye removal through both adsorption and catalytic mechanisms. According to,<sup>14</sup> Fe-based systems provide tunable active sites, whereas TiO<sub>2</sub> contributes surface reactivity and photocatalytic functionality. A study conducted by ref. 15 reported that carbonaceous materials further strengthen interfacial interactions and dye affinity when integrated with metal oxides. Despite these advantages, most studies evaluate isolated adsorbents or final membrane formulations without systematically resolving adsorption and pressure driven separation. As reported by ref. 16, existing PVDF/TiO<sub>2</sub> membranes could improve permeability, rejection, and antifouling, yet mechanistic contributions remain insufficiently investigated. An important unresolved issue is the progressive influence of TiO<sub>2</sub> and carbonaceous modifiers on adsorption–separation behaviour within nanocellulose modified PVDF membranes.

Nanocellulose (NC) is a promising bio-derived filler for PVDF membranes because its hydroxyl-rich structure can increase surface polarity, water affinity and membrane–dye interaction.<sup>17–20</sup> NC can also affect phase inversion by modifying polymer–solvent–nonsolvent exchange, thereby influencing pore formation, porosity and adsorption-site exposure. Nevertheless, NC loading must be controlled because excessive incorporation may cause filler aggregation, pore disruption and reduced accessibility of functional domains.<sup>20</sup> The optimisation of NC content is therefore necessary to establish a balance between improved hydrophilicity, structural integrity and adsorption functionality. Further modification with TiO<sub>2</sub> and carbon-based fillers can introduce complementary dye-removal pathways. TiO<sub>2</sub> contributes hydroxylated inorganic sites and photocatalytic activity, whereas graphene provides graphitic domains that may strengthen interaction with aromatic dye molecules through  $\pi$ – $\pi$  association.<sup>21–24</sup> Graphene oxide-derived modified hybrid material (GO-mHM) can further improve surface polarity and interfacial compatibility through

oxygen-containing functional groups.<sup>25</sup> Nevertheless, excessive loading of these fillers may reduce membrane performance through particle crowding, nanosheet restacking, pore obstruction, uncontrolled pore enlargement or non-uniform filler distribution. Thus, the main design requirement is not maximum filler incorporation, but the identification of a functional loading range where active domains remain dispersed, accessible and structurally compatible within the PVDF matrix.

A major limitation in many hybrid membrane studies is the separation of membrane-performance analysis from adsorption analysis. Membrane studies commonly emphasise water flux, dye rejection, flux recovery and antifouling performance, whereas adsorption studies often focus mainly on kinetic and isotherm fitting. This separation is inadequate for adsorptive hybrid membranes because dye removal occurs through coupled adsorption–separation behaviour. A membrane with high permeability may show poor retention if excessive pore enlargement lowers solute residence time and weakens selectivity.<sup>26</sup> Conversely, a membrane with strong dye affinity may suffer from poor permeability or irreversible fouling if dye molecules accumulate within poorly connected or blocked pore domains.<sup>27</sup> Effective hybrid membrane design therefore requires an optimum balance among permeability, surface heterogeneity, adsorption-site accessibility and reversible dye retention. To address this limitation, the present study evaluates MB adsorption across a sequential PVDF-based membrane development pathway, from pristine PVDF to PVDF–NC, PVDF/NC/TiO<sub>2</sub>, PVDF/NC/TiO<sub>2</sub>/GR and PVDF/NC/TiO<sub>2</sub>/GO-mHM membranes. This sequential framework allows the contribution of each modification stage to be examined under a consistent adsorption basis while linking the kinetic and equilibrium adsorption behaviour to membrane-separation performance. The comparison between GR and GO-mHM within the same PVDF/NC/TiO<sub>2</sub> platform further clarifies how graphitic interaction, oxygenated functional groups and filler compatibility influence MB uptake and adsorption-site accessibility. In this membrane system, MB removal is considered to arise from the combined effects of pore-mediated transport, surface adsorption and filler-induced interfacial interactions. NC may improve hydrophilic domain formation, TiO<sub>2</sub> may introduce hydroxylated inorganic adsorption sites, GR may enhance graphitic dye association,<sup>28,29</sup> and GO-mHM may provide oxygenated adsorption domains with improved interfacial compatibility.<sup>17,21,30</sup> However, these contributions are strongly dependent on filler loading, as excessive incorporation can promote agglomeration, restacking, or structural disturbance, thereby reducing the effective accessibility of adsorption sites.

Previous studies have reported that the incorporation of nanocellulose, TiO<sub>2</sub>, graphene and graphene-based materials could enhance the hydrophilicity, pore characteristics, permeability, dye rejection, antifouling behaviour and adsorption performance of PVDF-based membranes.<sup>31–34</sup> Although these studies provide substantial breadth in demonstrating the functional benefits of individual fillers and membrane formulations, comparatively, less attention has been given to the progressive evolution of adsorption behaviour across successive stages of membrane modification. In particular, kinetic

modelling has not been systematically applied to resolve the effects of sequential functionalization on adsorption rate, adsorption-site accessibility, surface heterogeneity and their relationship with membrane transport and dye separation. This gap is scientifically crucial because filler incorporation simultaneously alters membrane surface chemistry, pore structure, solute transport and filler dispersion, which collectively influence the availability and effectiveness of adsorption sites. Sequential kinetic evaluation is necessary to distinguish adsorption improvements associated with enhanced functional-site accessibility from apparent methylene blue dye retention arising primarily from structural effects such as pore obstruction, aggregation or restacking.

Accordingly, this study aims to evaluate the kinetic and equilibrium behaviour of methylene blue (MB) adsorption by sequentially modified polyvinylidene fluoride (PVDF)-based hybrid membranes incorporating nanocellulose (NC), titanium dioxide ( $\text{TiO}_2$ ), graphene (GR) and graphene oxide-derived modified hybrid material (GO-mHM). Specifically, the study identifies the most suitable kinetic model, determines the optimum filler loading at each membrane modification stage, compares homogeneous and heterogeneous isotherm models, distinguishes statistical model fit from physical parameter validity, and establishes the relationship between adsorption behaviour and membrane separation performance. This framework provides a mechanistic basis for designing adsorption-assisted PVDF hybrid membranes in which permeability, surface heterogeneity, filler dispersion and adsorption-site accessibility jointly control dye-removal performance. Overall, this study advances the depth and breadth of current knowledge by using kinetic modelling to explain the

relationship between sequential PVDF functionalisation, adsorption-site accessibility, surface heterogeneity and MB separation performance.

## 2 Material and methods

### 2.1 Materials

Four series of membrane groups were evaluated, specifically, pristine PVDF and NC-incorporated PVDF membranes,  $\text{TiO}_2$ -modified PVDF/NC membranes, GR-incorporated PVDF/NC/ $\text{TiO}_2$  membranes, and GO-mHM-incorporated PVDF/NC/ $\text{TiO}_2$  membranes. This staged design enabled comparison of adsorption behaviour across increasing levels of membrane functionalisation, from the unmodified PVDF matrix to carbon-based hybrid membranes containing either graphitic or oxygenated graphene-derived domains. The adsorption study was designed around a sequential membrane development framework, as illustrated by Fig. 1. The development sequence progressed from pristine PVDF to NC-incorporated PVDF membranes, followed by  $\text{TiO}_2$ -modified membranes, GR-modified membranes, and GO-mHM-modified membranes. At each stage, the optimum membrane from the preceding stage was used as the baseline for subsequent modification.

### 2.2 Preparation of bamboo-derived nanocellulose

Bamboo-derived nanocellulose was prepared from *Gigantochloa scortechinii* through sequential chemical pretreatment and mechanical size reduction as described in previous work.<sup>20</sup> The bamboo culms were cleaned, cut, ground and sieved before chemical treatment. Dewaxing was first carried out using a toluene-ethanol mixture to remove waxes, oils and extractives

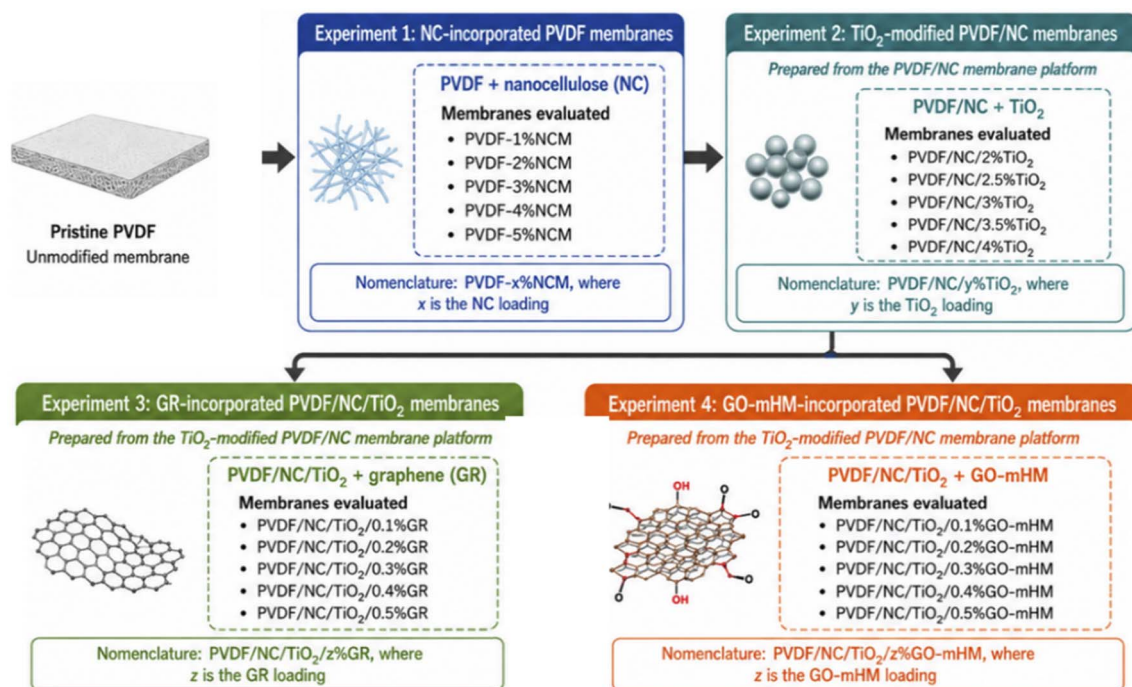


Fig. 1 Schematic illustration of the sequential membrane modification pathway and membrane nomenclature adopted in this study.

from the bamboo fibres. The dewaxed fibres were then subjected to delignification using acetic acid and hydrogen peroxide to remove lignin and expose the cellulose-rich fraction. Mercerisation was subsequently conducted using sodium hydroxide solution to reduce hemicellulose and residual non-cellulosic constituents. The purified cellulose was dried and then subjected to mechanical ball milling using a planetary ball mill. Milling was conducted at 250 rpm for two cycles to reduce the cellulose particles from the microscale to the nanoscale. The resulting bamboo-derived nanocellulose was used as the bio-based filler in the PVDF membrane formulations.

### 2.3 Preparation of GO-mHM

GO-mHM was synthesised from graphene nanopowder through a modified Hummers oxidation route adapted from the procedure reported by.<sup>35</sup> In this study, graphene nanopowder was first dispersed in a strongly acidic oxidation medium containing concentrated nitric acid and sulfuric acid and continuously stirred to promote uniform contact between the graphene particles and the reaction medium. This oxidation treatment was intended to modify the initially graphitic material by introducing oxygen containing functionalities and increasing the polarity of the graphene derived surface, thereby improving its compatibility with the hydrophilic components of the subsequent PVDF/NC/TiO<sub>2</sub> membrane system. Following completion of the oxidation stage, deionised water was gradually introduced into the reaction mixture to dilute the acidic suspension while maintaining controlled mixing. The resulting suspension was subsequently neutralised to approximately pH 7 through the gradual addition of sodium hydroxide solution. Neutralisation was performed carefully to minimise abrupt changes in the reaction environment and to facilitate subsequent purification of the oxidised graphene derived material. The solid product was then subjected to repeated washing with deionised water to remove residual acidic species, soluble reaction by products and remaining neutralisation products. After washing, the GO-mHM material was recovered by filtration and dried overnight to remove residual moisture. Then, the dried product was subsequently ground into a fine powder to improve particle uniformity and facilitate its dispersion during membrane dope preparation. The resulting GO-mHM was therefore obtained as an oxygenated graphene-based filler intended to provide chemically distinct interfacial regions within the PVDF/NC/TiO<sub>2</sub> matrix. Its incorporation was designed to complement the hydroxyl rich NC and TiO<sub>2</sub> components by introducing additional oxygen bearing and residual graphitic domains that could influence membrane polarity, filler matrix compatibility and the accessibility of dye interacting regions. The prepared GO-mHM powder was subsequently incorporated at the specified loading levels into the selected PVDF/NC/TiO<sub>2</sub> membrane formulation for fabrication of the final GO-mHM modified membrane series. Accordingly, the prepared GO-mHM was introduced as the fourth stage of sequential membrane modification into the selected PVDF/NC/TiO<sub>2</sub> formulation, enabling systematic evaluation of how oxygenated graphene derived domains

influenced MB adsorption relative to the corresponding graphene modified membrane system.

### 2.4 Membrane fabrication by phase inversion

All membranes were fabricated using the non-solvent induced phase separation (NIPS) method, following a procedure similar to that reported in previous study.<sup>20,26,36</sup> Briefly, LiCl was first dissolved in DMAc, followed by the addition and dispersion of the selected fillers. PVDF pellets were then gradually added into the solution and dissolved under continuous stirring to form a homogeneous casting dope. Approximately 10 mL of the dope solution was cast on a clean glass plate using a stainless-steel casting rod. The wet film was immediately immersed in a deionised water coagulation bath to initiate phase separation and membrane solidification. The membrane was then transferred to a second water bath for further removal of solvent and additives, then stored in deionised water at 5 °C prior to testing. The adsorption evaluation was designed using four sequential membrane groups. The membrane formulations were organised into four experimental groups. Experiment 1 comprised pristine PVDF and PVDF membranes containing different NC loadings. Experiment 2 consisted of TiO<sub>2</sub>-modified PVDF/NC membranes developed using the optimum PVDF/NC formulation identified in Experiment 1 as the baseline. Experiment 3 comprised GR-incorporated PVDF/NC/TiO<sub>2</sub> membranes, whereas Experiment 4 consisted of GO-mHM-incorporated PVDF/NC/TiO<sub>2</sub> membranes. This staged design enabled the adsorption behaviour to be compared from the unmodified PVDF matrix to carbon-based hybrid membranes containing either graphitic or oxygenated graphene-derived domains. The corresponding loading percentages for all membrane formulations are presented in Tables 1–4.

### 2.5 Membrane filtration performance

Membrane filtration performance was evaluated to provide separation-related context for the adsorption analysis similar to that reported in previous study.<sup>20,26,36</sup> Pure water flux was measured using a filtration system. Each membrane was compacted at 2 bar for 30 min before the operating pressure was reduced to 1 bar. Permeate was collected at 10 min intervals over a total filtration period of 70 min. Pure water flux was calculated from the permeate volume, effective membrane area and filtration time. MB dye rejection was evaluated using aqueous MB solutions with initial concentrations of 1, 2, 3, 4 and 5 ppm. The 1 to 5 mg per L MB concentration range was

Table 1 Membrane formulations and component loadings for Experiment 1

| Membrane    | PVDF (wt%) | DMAc (wt%) | LiCl (wt%) | NC (wt%)   |
|-------------|------------|------------|------------|------------|
| PVDF        | 15         | 84.66      | 0.34       | —          |
| PVDF-1% NCM | 15         | 84.51      | 0.34       | 1% of PVDF |
| PVDF-2% NCM | 15         | 84.36      | 0.34       | 2% of PVDF |
| PVDF-3% NCM | 15         | 84.21      | 0.34       | 3% of PVDF |
| PVDF-4% NCM | 15         | 84.06      | 0.34       | 4% of PVDF |
| PVDF-5% NCM | 15         | 83.91      | 0.34       | 5% of PVDF |

Table 2 Membrane formulations and component loadings for Experiment 2

| Membrane                      | PVDF (wt%) | DMAc (wt%) | LiCl (wt%) | NC (wt%) | TiO <sub>2</sub> (wt%) |
|-------------------------------|------------|------------|------------|----------|------------------------|
| PVDF-4% NCM                   | 15         | 84.06      | 0.34       | 0.6      | —                      |
| PVDF/NC/2.0% TiO <sub>2</sub> | 15         | 83.76      | 0.34       | 0.6      | 2.0% of PVDF           |
| PVDF/NC/2.5% TiO <sub>2</sub> | 15         | 83.69      | 0.34       | 0.6      | 2.5% of PVDF           |
| PVDF/NC/3.0% TiO <sub>2</sub> | 15         | 83.61      | 0.34       | 0.6      | 3.0% of PVDF           |
| PVDF/NC/3.5% TiO <sub>2</sub> | 15         | 83.54      | 0.34       | 0.6      | 3.5% of PVDF           |
| PVDF/NC/4.0% TiO <sub>2</sub> | 15         | 83.46      | 0.34       | 0.6      | 4.0% of PVDF           |

Table 3 Membrane formulations and component loadings for Experiment 3

| Membranes                     | PVDF (wt%) | DMAc (wt%) | LiCl (wt%) | NC (wt%) | TiO <sub>2</sub> (wt%) | GR (wt%)     |
|-------------------------------|------------|------------|------------|----------|------------------------|--------------|
| PVDF-NC/TiO <sub>2</sub>      | 15         | 83.61      | 0.34       | 0.6      | 0.45                   | —            |
| PVDF-NC/TiO <sub>2</sub> /GR1 | 15         | 83.58      | 0.34       | 0.6      | 0.45                   | 0.1% of PVDF |
| PVDF-NC/TiO <sub>2</sub> /GR2 | 15         | 83.55      | 0.34       | 0.6      | 0.45                   | 0.2% of PVDF |
| PVDF-NC/TiO <sub>2</sub> /GR3 | 15         | 83.52      | 0.34       | 0.6      | 0.45                   | 0.3% of PVDF |
| PVDF-NC/TiO <sub>2</sub> /GR4 | 15         | 83.49      | 0.34       | 0.6      | 0.45                   | 0.4% of PVDF |
| PVDF-NC/TiO <sub>2</sub> /GR5 | 15         | 83.46      | 0.34       | 0.6      | 0.45                   | 0.5% of PVDF |

Table 4 Membrane formulations and component loadings for Experiment 4

| Membranes                             | PVDF (wt%) | DMAc (wt%) | LiCl (wt%) | NC (wt%) | TiO <sub>2</sub> (wt%) | GO-mHM (wt%) |
|---------------------------------------|------------|------------|------------|----------|------------------------|--------------|
| PVDF-NC/TiO <sub>2</sub>              | 15         | 83.61      | 0.34       | 0.6      | 0.45                   | —            |
| PVDF/NC/TiO <sub>2</sub> /0.1% GO-mHM | 15         | 83.58      | 0.34       | 0.6      | 0.45                   | 0.1% of PVDF |
| PVDF/NC/TiO <sub>2</sub> /0.2% GO-mHM | 15         | 83.55      | 0.34       | 0.6      | 0.45                   | 0.2% of PVDF |
| PVDF/NC/TiO <sub>2</sub> /0.3% GO-mHM | 15         | 83.52      | 0.34       | 0.6      | 0.45                   | 0.3% of PVDF |
| PVDF/NC/TiO <sub>2</sub> /0.4% GO-mHM | 15         | 83.49      | 0.34       | 0.6      | 0.45                   | 0.4% of PVDF |
| PVDF/NC/TiO <sub>2</sub> /0.5% GO-mHM | 15         | 83.46      | 0.34       | 0.6      | 0.45                   | 0.5% of PVDF |

selected to represent a low-concentration residual-dye treatment regime, with the developed membranes intended for potential application as a polishing platform rather than for direct treatment of highly concentrated dye baths. The feed and permeate concentrations were determined using UV-Vis spectrophotometry. MB removal efficiency was calculated using the concentration difference between the feed and permeate solutions (eqn (2.1)). These data were used to relate membrane-separation performance to adsorption behaviour.

$$R = \left(1 - \frac{C_p}{C_i}\right) \times 100 \quad (2.1)$$

where  $R$  is the MB removal efficiency or dye removal ratio (%),  $C_p$  is the MB concentration in the permeate ( $\text{mg L}^{-1}$ ), and  $C_i$  is the initial MB concentration in the feed solution ( $\text{mg L}^{-1}$ ). Since 1 ppm MB is equivalent to approximately  $1 \text{ mg L}^{-1}$  in aqueous solution, the feed concentration was expressed as  $1 \text{ mg L}^{-1}$  for calculation purposes.

## 2.6 Evaluation of MB adsorption kinetics and equilibrium behaviour on PVDF hybrid membranes

The adsorption of MB dye onto the developed membranes was investigated at 25 °C under controlled experimental conditions. In this stage, MB solutions with initial concentrations ranging

from 1 to 5 ppm were used in the adsorption experiments, and the residual MB concentrations in the permeate were quantified using UV-Vis spectrophotometric analysis. The concentration data obtained from the UV-Vis analysis were then used to calculate the adsorption capacity of the membranes for subsequent kinetic and isotherm model fitting following the approach reported by.<sup>37</sup> The area specific adsorption capacity of MB,  $q_e$ , was determined from the mass of dye removed from solution relative to the effective membrane area and expressed as  $\text{mg m}^{-2}$ , as shown by eqn (2.2).

$$q_{\text{exp}} = \frac{(C_0 - C_e)V}{A} \quad (2.2)$$

where,  $q_e$  is the experimental adsorption capacity at equilibrium ( $\text{mg m}^{-2}$ ),  $C_0$  is the initial MB concentration ( $\text{mg L}^{-1}$ ),  $C_e$  is the MB concentration at equilibrium ( $\text{mg L}^{-1}$ ),  $V$  is the solution volume (L), and  $A$  is the effective membrane area ( $\text{m}^2$ ). Adsorption capacity was normalised to the effective membrane area and expressed as  $\text{mg m}^{-2}$  because the developed materials function as planar separation membranes rather than as dispersed particulate adsorbents. In conventional batch adsorption studies involving powders, beads or granular sorbents, adsorption capacity is commonly normalised to adsorbent mass and expressed as  $\text{mg g}^{-1}$ . In the present membrane system, however, MB uptake occurs within a defined active membrane area that

simultaneously governs solute contact, permeation and separation. Area based normalisation therefore provides a direct basis for comparing adsorption behaviour among membrane formulations tested under the same filtration geometry and is consistent with the area dependent description of membrane transport performance. Additionally, the reported  $\text{mg m}^{-2}$  values represent area specific adsorption capacity and should not be interpreted as directly equivalent to the mass specific capacities commonly reported for conventional adsorbents.

The adsorption kinetic behaviour was evaluated using the pseudo-first order (PFO) and pseudo-second order (PSO) models, while the equilibrium adsorption behaviour was analysed using the Langmuir and Freundlich isotherm models. These models were selected to provide a comparative assessment of MB adsorption behaviour under different assumptions related to adsorption rate, surface homogeneity and heterogeneity, and adsorption site distribution. The following procedures were carried out to formulate the adsorption models and evaluate MB uptake by the developed membranes, as shown by Table 5.

The kinetic and equilibrium adsorption models were fitted to the experimental data using non-linear regression based on the original mathematical forms. The corresponding linearized equations are presented only to provide the conventional mathematical representations of the respective models and were not used for final parameter estimation. The non-linear kinetic models were fitted directly to the experimental  $q_t$  against  $t$  data, whereas the non-linear equilibrium models were fitted directly to the experimental  $q_e$  against  $C_e$  data. The resulting non-linear regression parameters and predicted adsorption capacities were subsequently used for statistical evaluation and mechanistic interpretation. The adsorption experiments for each membrane formulation and initial MB concentration were performed in triplicate ( $n = 3$ ) under

identical experimental conditions to ensure the reproducibility of the measurements.

**2.6.1 Formulation of pseudo first order model.** The pseudo-first order (PFO) kinetic model is initially expressed in its differential form as shown in eqn (2.3). After integration, the model is represented by the non-linear expression in eqn (2.4) and the corresponding linearised form in eqn (2.5).<sup>38</sup> These equations were used to estimate the PFO rate constant,  $k_1$ , and to compare the experimental and calculated adsorption capacities. The PFO model was applied to evaluate whether the MB adsorption process was more strongly associated with the availability of active adsorption sites and the gradual occupation of adsorption domains on the membrane surface.<sup>39,40</sup> The coefficient of determination ( $R^2$ ) was subsequently used to assess the goodness of fit of the PFO model to the experimental adsorption kinetic data.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad (2.3)$$

$$q_t = q_e (1 - e^{-k_1 t}) \quad (2.4)$$

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (2.5)$$

where,  $q_t$  is the adsorption capacity at time  $t$  ( $\text{mg m}^{-2}$ ),  $k_1$  is the PFO adsorption rate constant ( $\text{min}^{-1}$ ) and  $t$  is the contact time or residence time (min). After integration, the PFO model is represented by the nonlinear expression in eqn (2.4), while its conventional linearised form is presented in eqn (2.5). Nonlinear regression of eqn (2.4) against the experimental  $q_t$  against  $t$  data was used to estimate  $q_e$  and  $k_1$ . Eqn (2.5) is provided only as the conventional linearised representation of the PFO model and was not used for final parameter estimation.

**2.6.2 Formulation of pseudo second order models.** The pseudo-second-order (PSO) kinetic model was used to describe

Table 5 Experimental conditions for dynamic MB adsorption evaluation

| Parameter                           | Experimental condition                                                      |
|-------------------------------------|-----------------------------------------------------------------------------|
| Adsorptive medium                   | Flat-sheet PVDF-based membrane                                              |
| Membrane dimension                  | Circular disc, 5.4 cm diameter                                              |
| Effective membrane area             | Approximately $22.9 \text{ cm}^2$ ( $2.29 \times 10^{-3} \text{ m}^2$ )     |
| Adsorbent dosage basis              | Effective membrane area rather than adsorbent mass                          |
| Membrane thickness                  | 0.04 mm                                                                     |
| Initial MB concentration, ( $C_0$ ) | 1, 2, 3, 4 and $5 \text{ mg L}^{-1}$                                        |
| MB solution volume                  | 3 L                                                                         |
| Solution Ph                         | Neutral (pH 7)                                                              |
| Temperature                         | $25^\circ \text{C}$                                                         |
| Operating pressure                  | 1 bar                                                                       |
| Agitation condition                 | No external mechanical agitation because mass transport was pressure-driven |
| Contact/filtration time             | 70 min                                                                      |
| Sampling interval                   | Every 10 min                                                                |
| Sample volume for UV-Vis analysis   | Approximately 5 mL                                                          |
| Methylene blue (MB) quantification  | UV-Vis spectrophotometry                                                    |
| Calibration range                   | 0.1–5.0 mg per L MB                                                         |
| Adsorption capacity basis           | Area-normalised, $\text{mg m}^{-2}$                                         |
| Adsorption capacity at time ( $t$ ) | $q_t = \frac{(C_0 - C_t)V}{A}$                                              |
| Equilibrium adsorption capacity     | $q_{\text{exp}} = \frac{(C_0 - C_e)V}{A}$                                   |

the MB adsorption kinetics of the developed membranes, with the fitted parameters used to evaluate equilibrium adsorption capacity, adsorption rate behaviour and adsorption-site accessibility. This model describes the adsorption rate as a function of the remaining available adsorption sites, where the rate is proportional to the square of the unoccupied adsorption capacity.<sup>39,41</sup> PSO model provides insight into whether MB uptake is strongly influenced by the availability of accessible adsorption sites and surface interaction within the membrane structure. The PSO kinetic model was first expressed in its differential form as displayed in eqn (2.6).<sup>42</sup> By integrating the equation using the boundary conditions  $q_t = 0$  at  $t = 0$  while  $q_t = q_e$  at a given time  $t$ , the non-linear form was obtained as presented in eqn (2.7). The corresponding linearised form is given in eqn (2.8). These expressions were used to estimate the PSO rate constant,  $k_2$ , and the calculated equilibrium adsorption capacity,  $q_e$ , which are subsequently used to evaluate the kinetic behaviour of MB adsorption onto the membrane surface. The coefficient of determination ( $R^2$ ) was subsequently used to assess the fit of the PSO model to the experimental adsorption kinetic data.

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad (2.6)$$

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2.7)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (2.8)$$

where,  $q_t$  is the adsorption capacity at time  $t$  ( $\text{mg m}^{-2}$ ),  $q_e$  is the equilibrium adsorption capacity ( $\text{mg m}^{-2}$ ),  $k_2$  is the PSO rate constant ( $\text{m}^2 \text{mg}^{-1} \text{min}^{-1}$ ) and  $t$  is the contact time or residence time (min). The nonlinear form of PSO model is presented in eqn (2.7), while eqn (2.8) represents its conventional linearized form. The experimental  $q_t$  against  $t$  data were fitted directly to eqn (2.7) using non-linear regression to estimate  $q_e$  and  $k_2$ . The linearized expression in eqn (2.8) is presented for mathematical reference only and was not used for final parameter estimation or model selection.

**2.6.3 Langmuir isotherm model.** The Langmuir adsorption isotherm was employed to determine the equilibrium adsorption behaviour of MB dye molecules onto the developed membranes using initial MB solute concentrations ranging from 1 to 5 ppm at 25 °C. This model assumes that adsorption occurs on a homogeneous membrane surface through monolayer coverage, where the available adsorption sites comprise a finite number of energetically uniform and identical active sites. This model also assumes that each adsorption site can accommodate one adsorbate molecule and that no significant interaction occurs between adsorbed molecules on neighbouring sites. The non-linear form of the Langmuir equation is expressed by eqn (2.9), while the corresponding linearised form is presented in eqn (2.10).<sup>43</sup> These equations were used to estimate the maximum monolayer adsorption capacity,<sup>44</sup>  $q_{\text{max}}$ , and the Langmuir adsorption constant,  $K_L$ , based on the slope and intercept generated from the linear plot of  $\frac{C_e}{q_e}$  against  $C_e$  for

evaluating the equilibrium adsorption behaviour of MB onto the membrane surface at different initial MB concentrations ranging from 1 to 5 ppm. The suitability of the Langmuir model was evaluated using the coefficient of determination,  $R^2$ , together with the physical relevance of the fitted parameters.

$$q_e = \frac{q_{\text{max}} K_L C_e}{1 + K_L C_e} \quad (2.9)$$

$$\frac{C_e}{q_e} = \frac{1}{q_{\text{max}}} C_e + \frac{1}{K_L q_{\text{max}}} \quad (2.10)$$

where  $q_e$  is the quantity of dye adsorbed per unit area of membrane at equilibrium ( $\text{mg m}^{-2}$ ),  $C_e$  is the concentration of MB dye at equilibrium ( $\text{mg L}^{-1}$ );  $q_{\text{max}}$  is the maximum monolayer adsorption capacity of MB on the membrane ( $\text{mg m}^{-2}$ ),  $K_L$  is the Langmuir constant ( $\text{L mg}^{-1}$ ) that reflects the affinity between MB molecules and the active sites. The non-linear form of the Langmuir isotherm is presented in eqn (2.9), while eqn (2.10) represents its conventional linearized form. The Langmuir parameters  $q_{\text{max}}$  and  $K_L$  were estimated by non-linear regression of eqn (2.9) directly against the experimental  $q_e$  against  $C_e$  data.

**2.6.4 Freundlich isotherm model.** The Freundlich isotherm model was also employed to determine the equilibrium adsorption behaviour of MB dye molecules onto the developed membranes at 25 °C. The analysis was conducted using initial MB concentrations ranging from 1 to 5 ppm to examine how the membrane adsorption capacity changed with increasing dye availability under equilibrium conditions. Unlike the Langmuir model, which assumes monolayer adsorption on a homogeneous surface, the Freundlich model describes adsorption on energetically heterogeneous surfaces where adsorption sites are not uniform and multilayer adsorption may occur. The non-linear expression of the Freundlich isotherm is given in eqn (2.11), while the corresponding linearised form is presented in eqn (2.12).<sup>45</sup> The Freundlich parameters,  $K_F$  and  $1/n$ , were obtained from the linear plot of  $\log q_e$  against  $\log C_e$ . The slope of the plot corresponds to  $1/n$ , while the intercept represents  $\log K_F$ . The obtained parameters were used to assess the heterogeneous adsorption behaviour of MB onto the membrane surface at different initial dye concentrations. The suitability of the Freundlich model was evaluated using the coefficient of determination ( $R^2$ ) together with the physical relevance of the fitted parameters and their consistency with the experimental adsorption data.

$$q_e = K_F C_e^{\frac{1}{n}} \quad (2.11)$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \quad (2.12)$$

where  $q_e$  is the quantity of dye adsorbed per unit area of the developed membrane at equilibrium ( $\text{mg m}^{-2}$ ),  $K_F$  is the Freundlich constant associated multilayer adsorption capacity ( $(\text{mg m}^{-2}) (\text{L mg}^{-1})^{1/n}$ ),  $C_e$  is the concentration of MB dye at equilibrium ( $\text{mg L}^{-1}$ ) and  $\frac{1}{n}$  is the Freundlich adsorption intensity. This linearised equation is used to estimate  $\frac{1}{n}$  and  $\log$

$K_F$  from the slope and intercept of the linear plot of  $\log q_e$  against  $\log C_e$ . The non-linear Freundlich expression presented in eqn (2.11) was fitted directly to the experimental  $q_e$  against  $C_e$  data using non-linear regression. The fitted parameters  $K_F$  and  $1/n$  were obtained without logarithmic transformation of the experimental adsorption data. Eqn (2.12) is retained only as the conventional linearized representation of the Freundlich model and was not used for final parameter estimation.

**2.6.5 Validation of adsorption kinetic and equilibrium isotherm models.** The goodness of fit of each adsorption kinetic and equilibrium isotherm model was evaluated using the coefficient of determination of regression analysis ( $R^2$ ) which reflects the degree of agreement between the experimental data and the model predictions. The mathematical expression for  $R^2$  is provided in eqn (2.13).<sup>46</sup>

$$R^2 = 1 - \frac{\sum_{i=1}^n (q_{e,\text{exp}} - q_{e,\text{model}})^2}{\sum_{i=1}^n (q_{e,\text{exp}} - \bar{q}_{e,\text{exp}})^2} \quad (2.13)$$

where  $q_{e,\text{exp}}$  is the experimental adsorption capacity at equilibrium ( $\text{mg m}^{-2}$ );  $q_{e,\text{model}}$  is the predicted adsorption capacity at equilibrium based on the isotherm model ( $\text{mg m}^{-2}$ );  $\bar{q}_{e,\text{exp}}$  is the mean of all experimentally observed values ( $\text{mg m}^{-2}$ ) and  $n$  is the total number of data points.

In general, an  $R^2$  value closer to 1 indicates stronger agreement between the experimental data and the fitted model. In this study, an  $R^2$  value greater than 0.75 was adopted as the minimum criterion for an acceptable model fit. This threshold indicates that the fitted model explains more than 75% of the variation in the experimental adsorption data, thereby supporting an acceptable level of agreement between the model prediction and the experimental results.<sup>47,48</sup> However, model suitability was not determined based on  $R^2$  alone. The agreement between experimental and calculated adsorption capacities, the physical relevance of the fitted parameters and the consistency of the model assumptions with the adsorption behaviour of MB on the developed membranes are also considered. The goodness of fit of each kinetic and equilibrium model was evaluated from the agreement between the experimental adsorption capacities and the corresponding values predicted by nonlinear regression. The coefficient of determination ( $R^2$ ) was employed as the principal statistical criterion for comparing the goodness of fit of the adsorption kinetic and equilibrium models. Model selection was not based solely on  $R^2$ , but also considered the agreement between experimental and model predicted adsorption capacities, the physical validity of the fitted parameters, and consistency with the underlying assumptions of each adsorption model.

## 3 Results and discussion

### 3.1 Adsorption–separation interpretation of sequential PVDF-based hybrid membrane

The adsorption behaviour of MB was evaluated to establish the contribution of each membrane modification stage to adsorption-assisted separation. In functional hybrid membranes, dye removal requires an integrated interpretation

of water flux, dye rejection, and adsorption capacity. Instead, the observed MB retention is interpreted as arising from the combined influence of convective transport, pore mediated retention, surface adsorption, filler dispersion and the accessibility of dye interacting membrane regions. Although the present study does not independently resolve each molecular interaction, these contributions are evaluated through their consistency with the kinetic, equilibrium, loading dependent and membrane characterisation results. This interpretation is consistent with the conceptual framework of the study, in which adsorption kinetics and equilibrium behaviour are employed to elucidate the mechanisms governing membrane separation performance. The sequential membrane modification led to a progressive increase in the equilibrium adsorption capacity for MB. At an initial MB concentration of 5 ppm, the fitted PSO equilibrium capacity increased from 1049.79  $\text{mg m}^{-2}$  for pristine PVDF to 2080.69  $\text{mg m}^{-2}$  for PVDF-4% NCM. Subsequent incorporation of  $\text{TiO}_2$  increased the capacity to 2408.14  $\text{mg m}^{-2}$  in PVDF/NC/3.0%  $\text{TiO}_2$ . Further modification with GR and GO-mHM increased the corresponding values to 2442.68 and 2462.38  $\text{mg m}^{-2}$ , respectively. These results demonstrate the cumulative contribution of each stage of modification to the adsorption functionality of the PVDF membrane matrix.

The improvement was consistent with the complementary physicochemical characteristics introduced through sequential membrane modification. In previous work, the enhancement in membrane performance was attributed to the hydrophilic, hydroxylated, graphitic and oxygen-containing interfacial domains associated with NC,  $\text{TiO}_2$ , GR and GO-mHM, respectively.<sup>20,26,36</sup> The present findings extend that earlier analysis by quantitatively demonstrating that sequential modification progressively broadened the adsorption environment relative to pristine PVDF. Consequently, the hybrid membranes exhibited a greater diversity of accessible sites and interfacial interactions for MB adsorption. Fig. 2 compares pristine PVDF, PVDF-4% NCM, PVDF/NC/3.0%  $\text{TiO}_2$ , PVDF/NC/ $\text{TiO}_2$ /0.2% GR and PVDF/NC/ $\text{TiO}_2$ /0.3% GO-mHM. The figure provides an integrated overview of the adsorption enhancement achieved throughout

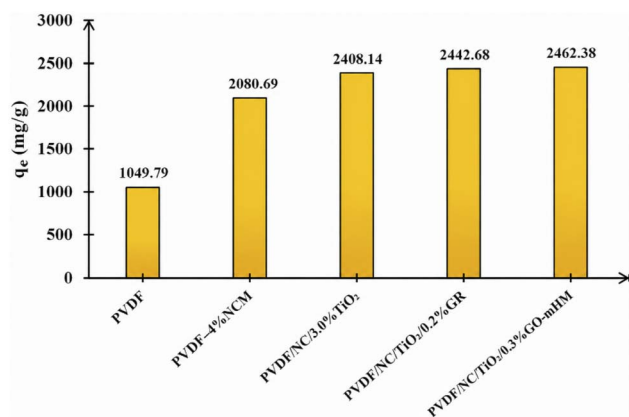


Fig. 2 Sequential variation in the fitted PSO equilibrium adsorption capacity at 5 ppm MB for the optimum membrane formulation obtained at each modification stage.

the sequential membrane-development pathway. A substantial increase occurred following NC incorporation, while subsequent  $\text{TiO}_2$ , GR and GO-mHM modifications produced further incremental improvements. Among the evaluated formulations, PVDF/NC/ $\text{TiO}_2$ /0.3% GO-mHM exhibited the highest fitted PSO equilibrium adsorption capacity.

The progressive increase in equilibrium adsorption capacity ( $q_e$ ) reflects the chemical and structural evolution of the membrane throughout the sequential modification process. The magnitude of improvement was governed by the availability, accessibility and distribution of the functional adsorption domains within the membrane structure. Each filler exhibited an optimum loading range that supported favourable dispersion, interfacial compatibility and adsorption site exposure. Higher loading levels promoted particle association, structural heterogeneity or restricted accessibility to functional sites, thereby influencing the effective adsorption response.<sup>49</sup> Comparable optimum-loading behaviour has been reported for PVDF-based and hybrid membrane systems. In these systems, membrane performance was primarily governed by filler dispersion, interfacial compatibility and the accessibility of functional domains.<sup>4,50–52</sup> Effective MB removal was achieved through a coordinated balance among permeability, accessible adsorption sites, surface heterogeneity and membrane selectivity.

### 3.2 Effect of NC loading and initial MB concentration on adsorption site accessibility and kinetic behaviour in PVDF–NC membranes

The adsorption kinetics of pristine PVDF and PVDF–NC membranes were evaluated using the pseudo first order (PFO) and pseudo second order (PSO) kinetic models. Table 3 summarises the fitted kinetic parameters obtained for pristine PVDF and PVDF–NC membranes at initial MB concentrations of 1–5 ppm. The parameters include the calculated equilibrium adsorption capacity ( $q_e$ ), PFO rate constant ( $k_1$ ), rate constants for PSO ( $k_2$ ) and the corresponding coefficients of determination ( $R^2$ ) values. Collectively, these parameters provide the basis for assessing model suitability, concentration-dependent MB uptake, and the influence of NC loading on adsorption behaviour. The kinetic comparison also establishes whether the optimum NC loading identified from membrane-separation performance corresponds with the adsorption response.

Across the pristine PVDF and PVDF–NC membrane series, the fitted  $q_e$  increased progressively as the initial MB concentration increased from 1 to 5 ppm as displayed in Table 6. A higher MB concentration generated a larger concentration gradient between the bulk solution and the membrane interface, thereby increasing the mass-transfer driving force and the availability of dye molecules near accessible adsorption sites. Huang and Shih (2025)<sup>53</sup> reported a comparable concentration-dependent increase in dye uptake, which they attributed to greater adsorbate availability at the adsorbent surface and a stronger concentration-driven transport force. The PSO model provided the most consistent kinetic representation of MB adsorption across the investigated membrane formulations.

The corresponding  $R^2$  values generally ranged from 0.96 to 0.98 throughout the membrane series and concentration range. By comparison, the fitting quality of the PFO model declined at higher NC loadings and MB concentrations, particularly for PVDF–3% NCM, PVDF–4% NCM, and PVDF–5% NCM. These results indicate that MB uptake became increasingly dependent on the equilibrium adsorption capacity and the progressive occupation of accessible adsorption domains as the PVDF matrix acquired greater surface functionality. Comparable kinetic behaviour has been reported for MB adsorption by nanocellulose-containing membranes, for which the pseudo-second-order model provided a better representation of the adsorption data.<sup>54,55</sup>

The strong PSO fit requires a mechanistically cautious interpretation. Agreement with the PSO model represents the dependence of the adsorption rate on equilibrium capacity and site occupation, rather than direct evidence of chemisorption.<sup>56</sup> Dye retention in PVDF-based hybrid membranes may arise from several simultaneous contributions, including electrostatic attraction, hydrogen bonding, interaction with functional surface domains,  $\pi$ – $\pi$  association, pore-assisted retention, and transport-induced delay within the membrane structure.<sup>57,58</sup> The PSO model serves as an empirical description of capacity-dependent MB uptake and progressive occupation of accessible adsorption regions. A consistent relationship between  $q_e$  and the PSO  $k_2$  was observed throughout the membrane groups. The  $q_e$  increased with initial MB concentration, whereas  $k_2$  generally decreased. These trends represent complementary kinetic responses. A higher MB concentration increases the total number of dye molecules available for adsorption and consequently raises the final uptake capacity. Simultaneously, the greater dye loading intensifies competition for finite adsorption sites and extends the time required for MB molecules to access less readily available regions. A study reported a similar increase in MB adsorption capacity accompanied by a decrease in the PSO rate constant.<sup>59</sup> Another study likewise observed increasing  $q_e$  and decreasing  $k_2$  with increasing MB concentration, with intraparticle diffusion contributing to the overall adsorption process.<sup>60</sup> Accordingly,  $q_e$  and  $k_2$  require concurrent interpretation because the rate constant alone provides an incomplete measure of adsorption performance.

NC incorporation substantially enhanced MB adsorption relative to pristine PVDF. Based on the PSO parameters in Table 3, the  $q_e$  value at 5 ppm MB increased from 1049.79  $\text{mg m}^{-2}$  for pristine PVDF to 1187.86, 1329.62, 1565.14, and 2080.69  $\text{mg m}^{-2}$  for PVDF–1% NCM, PVDF–2% NCM, PVDF–3% NCM, and PVDF–4% NCM, respectively. At 5% NC loading, the equilibrium capacity reached 1821.22  $\text{mg m}^{-2}$ . The resulting profile identifies 4% NC as the optimum loading for maximising MB adsorption within the PVDF–NC membrane series. The enhancement achieved between pristine PVDF and PVDF–4% NCM originated from the hydroxyl-rich and hydrophilic structure of NC. Incorporation of NC increased membrane polarity and wettability while introducing oxygen-containing functional domains capable of interacting with MB.<sup>61,62</sup> These physico-chemical changes expanded the number and accessibility of adsorption active regions located on the external membrane

**Table 6** PFO and PSO kinetic parameters for MB adsorption onto pristine PVDF and PVDF–NC membranes at different initial MB concentrations

| Kinetic model | Membrane    | Parameters                                                 | Initial MB concentration (ppm) |                       |                       |                       |                       |
|---------------|-------------|------------------------------------------------------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|               |             |                                                            | 1                              | 2                     | 3                     | 4                     | 5                     |
| PFO           | Pristine    | $q_e$ (mg m <sup>-2</sup> )                                | 158.43                         | 347.61                | 546.52                | 789.96                | 993.96                |
|               |             | $k_1$ (min <sup>-1</sup> )                                 | 0.0903                         | 0.0895                | 0.0862                | 0.0943                | 0.0954                |
|               |             | $R^2$                                                      | 0.98                           | 0.96                  | 0.98                  | 0.94                  | 0.94                  |
|               | PVDF–1% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 190.81                         | 409.62                | 648.27                | 870.37                | 1086.21               |
|               |             | $k_1$ (min <sup>-1</sup> )                                 | 0.0962                         | 0.0782                | 0.0924                | 0.0986                | 0.0872                |
|               |             | $R^2$                                                      | 0.98                           | 0.99                  | 0.95                  | 0.97                  | 0.98                  |
|               | PVDF–2% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 223.37                         | 486.22                | 751.66                | 953.28                | 1194.45               |
|               |             | $k_1$ (min <sup>-1</sup> )                                 | 0.1008                         | 0.0864                | 0.0976                | 0.0820                | 0.0828                |
|               |             | $R^2$                                                      | 0.98                           | 0.97                  | 0.93                  | 0.98                  | 0.98                  |
|               | PVDF–3% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 266.57                         | 565.13                | 888.19                | 1247.08               | 1528.05               |
|               |             | $k_1$ (min <sup>-1</sup> )                                 | 0.1083                         | 0.0938                | 0.0998                | 0.1101                | 0.1032                |
|               |             | $R^2$                                                      | 0.98                           | 0.95                  | 0.91                  | 0.84                  | 0.89                  |
|               | PVDF–4% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 376.58                         | 783.03                | 1237.31               | 1652.88               | 2066.16               |
|               |             | $k_1$ (min <sup>-1</sup> )                                 | 0.1185                         | 0.0959                | 0.1079                | 0.1085                | 0.1076                |
|               |             | $R^2$                                                      | 0.97                           | 0.93                  | 0.86                  | 0.85                  | 0.86                  |
|               | PVDF–5% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 321.39                         | 674.05                | 1062.09               | 1449.94               | 1794.50               |
|               |             | $k_1$ (min <sup>-1</sup> )                                 | 0.1140                         | 0.0950                | 0.1043                | 0.1092                | 0.1057                |
|               |             | $R^2$                                                      | 0.97                           | 0.94                  | 0.88                  | 0.85                  | 0.88                  |
| PSO           | Pristine    | $q_e$ (mg m <sup>-2</sup> )                                | 171.81                         | 375.98                | 599.50                | 837.94                | 1049.79               |
|               |             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $7.47 \times 10^{-4}$          | $3.09 \times 10^{-4}$ | $1.90 \times 10^{-4}$ | $1.43 \times 10^{-4}$ | $1.15 \times 10^{-4}$ |
|               |             | $R^2$                                                      | 0.97                           | 0.97                  | 0.97                  | 0.96                  | 0.96                  |
|               | PVDF–1% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 203.82                         | 465.18                | 693.11                | 950.96                | 1187.86               |
|               |             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $7.20 \times 10^{-4}$          | $2.30 \times 10^{-4}$ | $1.71 \times 10^{-4}$ | $1.20 \times 10^{-4}$ | $9.90 \times 10^{-5}$ |
|               |             | $R^2$                                                      | 0.97                           | 0.97                  | 0.96                  | 0.97                  | 0.97                  |
|               | PVDF–2% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 236.08                         | 532.76                | 786.87                | 1064.28               | 1329.62               |
|               |             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $6.85 \times 10^{-4}$          | $2.14 \times 10^{-4}$ | $1.55 \times 10^{-4}$ | $1.04 \times 10^{-4}$ | $8.39 \times 10^{-5}$ |
|               |             | $R^2$                                                      | 0.97                           | 0.97                  | 0.96                  | 0.97                  | 0.97                  |
|               | PVDF–3% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 277.36                         | 600.65                | 921.67                | 1244.08               | 1565.14               |
|               |             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $6.72 \times 10^{-4}$          | $1.99 \times 10^{-4}$ | $1.34 \times 10^{-4}$ | $1.04 \times 10^{-4}$ | $8.00 \times 10^{-5}$ |
|               |             | $R^2$                                                      | 0.98                           | 0.96                  | 0.96                  | 0.96                  | 0.96                  |
|               | PVDF–4% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 384.17                         | 825.35                | 1244.35               | 1658.87               | 2080.69               |
|               |             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $5.75 \times 10^{-4}$          | $1.46 \times 10^{-4}$ | $1.03 \times 10^{-4}$ | $7.73 \times 10^{-5}$ | $6.14 \times 10^{-5}$ |
|               |             | $R^2$                                                      | 0.98                           | 0.96                  | 0.96                  | 0.96                  | 0.96                  |
|               | PVDF–5% NCM | $q_e$ (mg m <sup>-2</sup> )                                | 330.70                         | 712.99                | 1082.98               | 1451.47               | 1821.22               |
|               |             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $6.22 \times 10^{-4}$          | $1.69 \times 10^{-4}$ | $1.16 \times 10^{-4}$ | $8.86 \times 10^{-5}$ | $7.01 \times 10^{-5}$ |
|               |             | $R^2$                                                      | 0.98                           | 0.96                  | 0.96                  | 0.96                  | 0.96                  |

surface and along the pore walls. Comparable improvements have been reported for nanocellulose-incorporated and hybrid PVDF membranes, although earlier studies have frequently focused on permeability, rejection, or overall removal efficiency rather than systematic kinetic comparison across multiple filler loadings.<sup>4,9,36,63</sup> The lower  $q_e$  recorded for PVDF–5% NCM indicates that the adsorption benefit reached a structural threshold beyond 4% NC loading. At elevated NC content, strong intermolecular hydrogen bonding between adjacent hydroxyl-rich particles can promote partial aggregation, local pore perturbation, and reduced structural uniformity.<sup>20</sup> These effects decrease the exposed interfacial area of NC and restrict MB transport towards available adsorption domains. Another study similarly associated excessive nanocellulose loading with aggregation arising from intermolecular hydrogen bonding.<sup>64</sup> Related studies on.<sup>4,50</sup>

The PVDF–NC series therefore establishes the first adsorption–separation optimisation within the sequential membrane-development pathway. Moderate NC incorporation increased adsorption capacity by expanding the population of hydrophilic

and hydroxyl-rich interaction sites. Further addition shifted the membrane towards greater particle association and lower effective site exposure. These findings support the selection of PVDF–4% NCM as the optimum NC-incorporated formulation for subsequent TiO<sub>2</sub> modification. More broadly, the results demonstrate that adsorption capacity is governed by the spatial accessibility and distribution of functional domains within the membrane matrix.

### 3.3 Equilibrium adsorption behaviour of pristine PVDF and PVDF–NCM

The equilibrium adsorption behaviour of pristine PVDF and PVDF–NC membranes was evaluated using the Langmuir and Freundlich isotherm models. Table 7 summarises the fitted parameters for the PVDF–NC membrane series, including the Langmuir  $q_{\max}$  and  $K_L$ , Freundlich  $K_F$  and  $(1/n)$ , together with their respective  $R^2$  values. The parameter set enables evaluation of statistical fitting quality alongside physical model validity. The corresponding nonlinear fitted Langmuir and Freundlich curves are presented in Fig. 3 to 4, respectively, to compare the

Table 7 Langmuir and Freundlich isotherm parameters for MB adsorption onto pristine PVDF and PVDF–NC membranes

| Membranes   | Langmuir                         |                             |       | Freundlich                                                       |       |       |
|-------------|----------------------------------|-----------------------------|-------|------------------------------------------------------------------|-------|-------|
|             | $q_{\max}$ (mg m <sup>-2</sup> ) | $K_L$ (L mg <sup>-1</sup> ) | $R^2$ | $K_F$ (mg m <sup>-2</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup> | 1/n   | $R^2$ |
| Pristine    | −1428.57                         | −0.159                      | 0.79  | 250.32                                                           | 0.818 | 0.99  |
| PVDF-1% NCM | −3333.33                         | −0.094                      | 0.99  | 344.51                                                           | 0.872 | 0.99  |
| PVDF-2% NCM | −10000                           | −0.044                      | 0.99  | 456.25                                                           | 0.919 | 0.99  |
| PVDF-3% NCM | −10000                           | −0.059                      | 0.97  | 672.98                                                           | 0.878 | 0.99  |
| PVDF-4% NCM | −50000                           | −0.04                       | 0.99  | 2232.03                                                          | 0.911 | 0.99  |
| PVDF-5% NCM | −20000                           | −0.05                       | 0.97  | 1142.62                                                          | 0.896 | 0.99  |

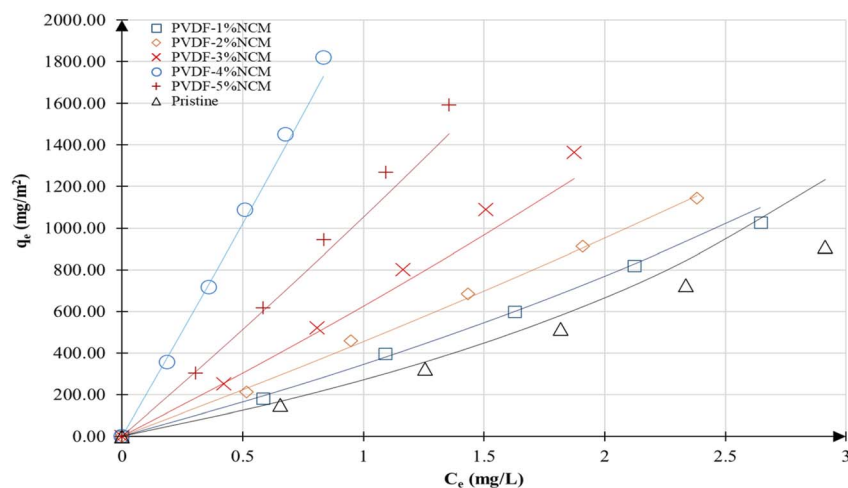


Fig. 3 Nonlinear Langmuir isotherm fitting for MB adsorption onto pristine PVDF and PVDF–NC membranes with different NC loadings at 25 °C.

experimentally determined adsorption capacities with the predictions of each equilibrium model. The fitted parameters reported in Table 7 were obtained directly from nonlinear regression of the original equilibrium equations. This distinction is essential because regression strength alone provides

limited evidence of model suitability or adsorption mechanism. As shown by the linearised Langmuir plots in Fig. 3, several membrane formulations produced apparently strong linear relationships. However, the fitted  $q_{\max}$  and  $K_L$  values were negative across the membrane series, despite the high  $R^2$

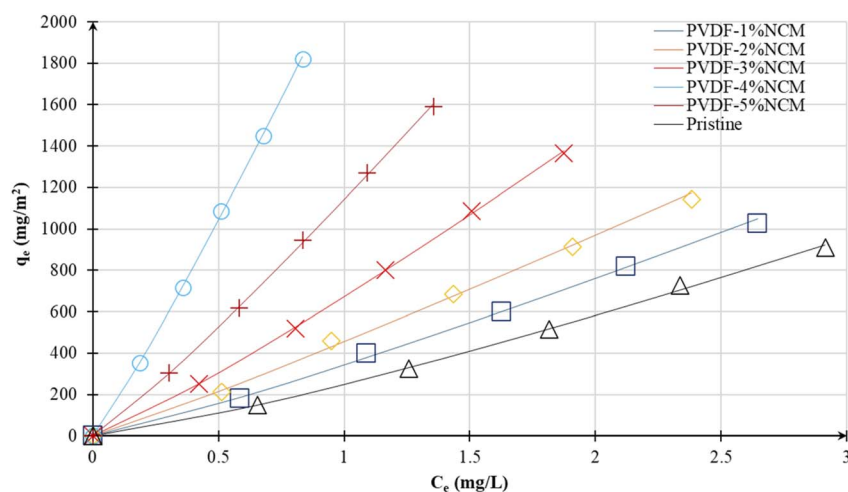


Fig. 4 Nonlinear Freundlich isotherm fitting for MB adsorption onto pristine PVDF and PVDF–NC membranes with different NC loadings at 25 °C.

values. Such values fall outside the physical constraints of monolayer capacity and adsorption affinity. Negative Langmuir constants are physically meaningless and indicate that the model assumptions do not adequately represent the adsorption system.<sup>65,66</sup> The Langmuir model provides a limited physical representation of MB adsorption by the PVDF-NC membranes, despite the apparently strong linear correlations observed in selected cases. This outcome illustrates the importance of assessing adsorption models through both statistical and physical criteria. Strong linear correlation provides meaningful model support only when the resulting parameters remain consistent with the underlying adsorption assumptions. The parameter behaviour observed in the present study indicates that MB uptake occurred across a heterogeneous population of adsorption domains rather than through ideal monolayer coverage of energetically equivalent sites. Such heterogeneity is plausible in PVDF-NC membranes because the hydrophobic PVDF matrix coexists with hydrophilic NC-rich domains bearing abundant surface hydroxyl groups, while NC incorporation modifies the membrane pore morphology and increases the available internal interfacial area.<sup>67</sup> These chemically and structurally different domains may provide distinct adsorption environments, consistent with the energetic heterogeneity represented by the Freundlich model.

The Freundlich model provided the most coherent equilibrium description of the PVDF-NC series as demonstrated by the highly linear regressions presented in Fig. 4 and the  $R^2$  value of 0.99 obtained across all formulations. The Freundlich  $K_F$  value increased from 250.32 for pristine PVDF to 2232.03 for PVDF-4% NCM, before reaching 1142.62 for PVDF-5% NCM. This variation closely follows the PSO equilibrium-capacity trend and identifies 4% NC as the loading that generated the most favourable heterogeneous adsorption environment. The reduction in the Freundlich  $K_F$  value from 2232.03 for PVDF-4% NCM to 1142.62 for PVDF-5% NCM was attributed to NC agglomeration at the excessive filler loading.<sup>20</sup> In the earlier study, the FESEM surface micrograph of PVDF-5% NCM revealed discrete, undissolved nanocellulose-rich agglomerates that were not observed at lower loadings, providing direct morphological evidence of reduced filler dispersion.<sup>20</sup> The corresponding cross-sectional image also exhibited distorted finger-like pores and a thicker sponge-like region, indicating that excessive nanocellulose increased dope-solution viscosity and disrupted phase-inversion kinetics. This interpretation was further supported by EDX analysis, which showed that the oxygen content decreased from  $36.81 \pm 2.98$  wt% for PVDF-4% NCM to  $27.62 \pm 1.64$  wt% for PVDF-5% NCM, despite the higher nominal NC loading.<sup>20</sup> At excessive loading, the shorter average separation between NC particles likely increased interparticle contact, enabling hydrogen bonding among surface hydroxyl groups and van der Waals attraction to promote and stabilise particle agglomeration.<sup>68–70</sup> The resulting agglomeration is consistent with less uniform NC distribution and reduced exposure of oxygen-rich NC domains within the local EDX sampling region, rather than a reduction in the total NC content of the membrane. Freundlich-dominant behaviour has also been reported for cellulose-based adsorbents and nanocellulose-

containing composites. Dye adsorption onto a modified cellulose nanofibre-reinforced hydrogel followed the Freundlich model, indicating adsorption across heterogeneous sites with non-uniform adsorption energies and possible multilayer uptake.<sup>71</sup> Similarly, methylene blue and basic violet 16 adsorption onto a polyurethane nanocomposite containing activated carbon and cellulose nanowhiskers followed the Freundlich isotherm and PSO kinetics.<sup>72</sup> Freundlich equilibrium behaviour and PSO kinetics were also reported for MB adsorption onto mesoporous nanocellulose- Hectorite-alginate beads.<sup>73</sup> Collectively, these studies support the suitability of the Freundlich model for cellulose-containing adsorbents with chemically and structurally heterogeneous adsorption environments.

### 3.4 PSO kinetic behaviour of TiO<sub>2</sub>, GR, and GO-mHM-incorporated membranes

Following optimisation of the PVDF-NC membrane, the kinetic assessment was extended to membranes incorporating TiO<sub>2</sub>, GR, and GO-mHM to determine the influence of sequential nanofiller addition on MB uptake. Each nanofiller introduced chemically distinct interfacial domains into the PVDF-NC matrix. TiO<sub>2</sub> introduced polar inorganic domains bearing surface Ti-OH groups. These hydroxyl groups influence TiO<sub>2</sub> surface wettability and can serve as interaction sites for MB through hydrogen bonding and electrostatic attraction.<sup>21,22</sup> GR supplied  $\pi$ -conjugated graphitic domains capable of associating with the planar aromatic structure of MB through non-covalent  $\pi$ - $\pi$  interactions.<sup>74</sup> GO-mHM introduced GO-derived domains containing oxygen-bearing functional groups, thereby increasing interfacial polarity and providing additional sites for MB uptake through electrostatic and  $\pi$ - $\pi$  interactions.<sup>75,76</sup> These compositional differences provided a physico-chemical basis for comparing the PSO kinetic behaviour of the TiO<sub>2</sub>-, GR-, and GO-mHM-incorporated membranes.

Across the TiO<sub>2</sub>, GR, and GO-mHM membrane groups, the PSO model consistently represented the adsorption data with  $R^2$  values generally approaching 0.98. For every membrane series,  $q_e$  increased as the initial MB concentration increased from 1 to 5 ppm, whereas  $k_2$  generally decreased. The increase in equilibrium adsorption capacity with increasing initial MB concentration was attributed to the greater quantity of dye available in the solution and the steeper concentration gradient established between the bulk solution and the membrane interface. The higher initial MB concentration established a stronger concentration gradient between the bulk solution and the membrane surface, thereby increasing the mass-transfer driving force towards accessible adsorption domains.<sup>77,78</sup> A comparable concentration-dependent response was reported for MB adsorption onto alkali-activated composite foams, where increasing the influent MB concentration increased the cumulative adsorption amount because of the enhanced concentration gradient and mass-transfer driving force.<sup>79</sup> The concurrent decrease in the PSO rate constant ( $k_2$ ) indicated that the normalised approach to equilibrium became slower as the initial MB concentration increased. This trend may indicate the preferential occupation of readily accessible

adsorption sites, followed by progressively slower transport towards less accessible pore-associated sites and internal interfacial regions. A cellulose-modified clay composite showed a similar increase in equilibrium capacity from 69.6 to 259.3 mg g<sup>-1</sup>, as the initial MB concentration increased from 50 to 250 mg L<sup>-1</sup>. Over the same concentration range, the fitted PSO rate constant decreased markedly overall, indicating that greater equilibrium uptake was accompanied by a lower apparent adsorption rate constant.<sup>80</sup>

Comparable concentration-dependent behaviour has been reported in MB adsorption studies, where higher initial dye concentrations increased  $q_e$  while reducing the PSO rate constant through boundary-layer resistance, adsorption-site competition, and diffusion constraints.<sup>59,60</sup> The two trends therefore represent different aspects of the same adsorption process. The equilibrium capacity quantifies the final quantity of retained MB, whereas  $k_2$  describes the apparent rate of approach towards that capacity under a specific set of experimental conditions. Meaningful kinetic comparison consequently requires considering both parameters together.

**3.4.1 Effect of TiO<sub>2</sub> incorporation on MB adsorption.** PVDF-4% NCM was identified as the optimum NC-incorporated membrane and subsequently used as the baseline formulation for evaluating TiO<sub>2</sub> incorporation. Table 8 presents the PSO kinetic parameters for PVDF-4% NCM and the TiO<sub>2</sub>-modified PVDF/NC membranes. These parameters facilitate comparison of adsorption capacity ( $q_e$ ), apparent kinetic response ( $k_2$ ), and goodness of fit ( $R^2$ ) across the membrane series. PVDF-4% NCM served as the reference formulation, while TiO<sub>2</sub> loading varied from 2.0% to 4.0% relative to PVDF mass.

Based on Table 8, at 5 ppm MB, the equilibrium capacity increased from 2080.69 mg m<sup>-2</sup> for PVDF-4% NCM to 2167.32, 2247.59, and 2408.14 mg m<sup>-2</sup> for PVDF/NC/2.0% TiO<sub>2</sub>, PVDF/NC/2.5% TiO<sub>2</sub>, and PVDF/NC/3.0% TiO<sub>2</sub>, respectively. The

corresponding  $q_e$  values for PVDF/NC/3.5% TiO<sub>2</sub> and PVDF/NC/4.0% TiO<sub>2</sub> were 2327.87 and 2087.05 mg m<sup>-2</sup>. This loading-dependent trend identifies 3.0% TiO<sub>2</sub> as the optimum loading for enhancing MB adsorption, consistent with the optimum previously reported for membrane separation performance.<sup>36</sup> Such enhancement at 3.0% TiO<sub>2</sub> arose from the complementary surface characteristics of NC and TiO<sub>2</sub>. NC established a hydrophilic polymer-filler framework containing hydroxyl-rich domains, while TiO<sub>2</sub> supplied hydroxylated inorganic surfaces and photoactive regions. Their combined incorporation increased membrane wettability and expanded the number of polar interaction sites accessible to MB. Hydration layers formed along the external surface and pore walls may also regulate dye interaction by maintaining an aqueous interfacial environment while permitting controlled retention through polar groups, hydroxylated TiO<sub>2</sub> surfaces, and accessible pore-wall domains.<sup>9,36</sup> Adsorption performance is influenced by the interplay among surface chemistry, functional-group accessibility, wettability, surface charge, pore structure, and operating conditions.<sup>81–84</sup>

At TiO<sub>2</sub> loadings above 3.0%, the membrane no longer exhibited proportional improvement in dye separation and antifouling performance. FESEM analysis revealed visible TiO<sub>2</sub>-rich accumulations on the surface of the PVDF/NC/4.0% TiO<sub>2</sub> membrane, while EDX recorded the highest Ti and O contents at this loading, indicating increasingly non-uniform nanoparticle distribution.<sup>20</sup> The mean pore size also increased from 4.70 μm at 3.0% TiO<sub>2</sub> to 4.79 and 4.93 μm at 3.5% and 4.0% TiO<sub>2</sub>, respectively, suggesting a loss of the pore refinement achieved at the optimum loading. These structural changes were accompanied by lower MB removal efficiency and slightly poorer antifouling performance, indicating that excessive TiO<sub>2</sub> promoted particle agglomeration and structural heterogeneity that reduced the effective utilisation of TiO<sub>2</sub>-containing

**Table 8** PSO kinetic model parameters for MB adsorption onto PVDF-4% NCM and TiO<sub>2</sub>-incorporated PVDF/NCM at varying initial MB concentrations and 25 °C

| Experiment 2: TiO <sub>2</sub> -incorporated membranes | Parameters                                                 | Initial MB concentration (ppm) |                       |                       |                       |                       |
|--------------------------------------------------------|------------------------------------------------------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                                                        |                                                            | 1                              | 2                     | 3                     | 4                     | 5                     |
| PVDF-4% NCM (baseline)                                 | $q_e$ (mg m <sup>-2</sup> )                                | 384.17                         | 825.35                | 1244.35               | 1658.87               | 2080.69               |
|                                                        | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.40 \times 10^{-4}$          | $1.46 \times 10^{-4}$ | $1.03 \times 10^{-4}$ | $7.73 \times 10^{-5}$ | $5.95 \times 10^{-5}$ |
|                                                        | $R^2$                                                      | 0.98                           | 0.96                  | 0.96                  | 0.96                  | 0.96                  |
| PVDF/NC/2% TiO <sub>2</sub>                            | $q_e$ (mg m <sup>-2</sup> )                                | 424.41                         | 854.03                | 1291.60               | 1729.19               | 2167.32               |
|                                                        | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.74 \times 10^{-4}$          | $1.57 \times 10^{-4}$ | $1.04 \times 10^{-4}$ | $7.73 \times 10^{-5}$ | $6.14 \times 10^{-5}$ |
|                                                        | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/2.5% TiO <sub>2</sub>                          | $q_e$ (mg m <sup>-2</sup> )                                | 444.62                         | 888.95                | 1342                  | 1794.89               | 2247.59               |
|                                                        | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.62 \times 10^{-4}$          | $1.50 \times 10^{-4}$ | $9.96 \times 10^{-5}$ | $7.45 \times 10^{-5}$ | $6.17 \times 10^{-5}$ |
|                                                        | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/3% TiO <sub>2</sub>                            | $q_e$ (mg m <sup>-2</sup> )                                | 485.04                         | 958.78                | 1441.61               | 1926.31               | 2408.14               |
|                                                        | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $5.75 \times 10^{-4}$          | $1.63 \times 10^{-4}$ | $9.31 \times 10^{-5}$ | $8.04 \times 10^{-5}$ | $6.41 \times 10^{-5}$ |
|                                                        | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/3.5% TiO <sub>2</sub>                          | $q_e$ (mg m <sup>-2</sup> )                                | 464.83                         | 923.86                | 1392.40               | 1860.6                | 2327.87               |
|                                                        | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.50 \times 10^{-4}$          | $1.45 \times 10^{-4}$ | $9.60 \times 10^{-5}$ | $7.19 \times 10^{-5}$ | $5.74 \times 10^{-5}$ |
|                                                        | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/4% TiO <sub>2</sub>                            | $q_e$ (mg m <sup>-2</sup> )                                | 404.20                         | 819.11                | 1241.20               | 1663.48               | 2087.05               |
|                                                        | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.88 \times 10^{-4}$          | $1.39 \times 10^{-4}$ | $1.08 \times 10^{-4}$ | $6.94 \times 10^{-5}$ | $5.55 \times 10^{-5}$ |
|                                                        | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |

interfacial regions.<sup>36</sup> Such changes reduced the effective exposure of adsorption domains despite the larger nominal TiO<sub>2</sub> content. A comparable non-linear loading response was observed in Eu-TiO<sub>2</sub> containing PVDF membranes, where excessive nanoparticle loading promoted agglomeration, reduced pore density and pore size, and consequently diminished dye adsorption capacity.<sup>85</sup> Other investigations have similarly shown that TiO<sub>2</sub> enhances PVDF membrane functionality, dye removal, and photocatalytic response when the nanoparticles remain well dispersed and effectively integrated within the polymer matrix.<sup>86</sup> Uniform dispersion and strong interfacial anchoring of TiO<sub>2</sub> nanoparticles within PVDF-based hybrid films enhanced MB degradation performance and operational reusability.<sup>87</sup> The concentration-dependent kinetic response remained consistent within the TiO<sub>2</sub> membrane series. For PVDF/NC/3.0% TiO<sub>2</sub>,  $q_e$  increased from 485.04 mg m<sup>-2</sup> at 1 ppm to 2408.14 mg m<sup>-2</sup> at 5 ppm, while  $k_2$  decreased. The increasing equilibrium capacity reflects greater MB availability and a stronger concentration gradient, whereas the decreasing rate constant reflects intensified competition for finite adsorption regions and slower access to less exposed sites. TiO<sub>2</sub> incorporation therefore enhanced adsorption-assisted separation by introducing accessible inorganic adsorption sites, provided that the nanoparticles remained well dispersed within an optimum loading range.

**3.4.2 Effect of GR incorporation on MB adsorption and membrane selectivity.** GR was incorporated into the PVDF/NC/3.0% TiO<sub>2</sub> baseline membrane to determine the contribution of graphitic carbon domains to MB uptake. Graphene can enhance dye adsorption through interactions with aromatic molecules, while its influence on pore development and membrane transport remains strongly dependent on loading and dispersion. The GR content ranged from 0.1% to 0.5% relative to the PVDF mass. Table 9 presents the PSO kinetic parameters

obtained for the baseline PVDF/NC/3.0% TiO<sub>2</sub> membrane and the GR-incorporated PVDF/NC/TiO<sub>2</sub> formulations. The values of  $q_e$ ,  $k_2$  and  $R^2$  define the relationship between GR loading, adsorption-site availability, and apparent kinetic behaviour across the investigated MB concentration range. At 5 ppm MB,  $q_e$  increased from 2408.14 mg m<sup>-2</sup> for the baseline membrane to 2414.23 and 2442.68 mg m<sup>-2</sup> for PVDF/NC/TiO<sub>2</sub>/0.1% GR and PVDF/NC/TiO<sub>2</sub>/0.2% GR, respectively. The increase at low GR loading indicates that graphitic adsorption regions were introduced while the accessibility of the existing NC and TiO<sub>2</sub> domains remained largely preserved. The optimum response at 0.2% GR represents a balance among graphitic interaction sites, accessible NC/TiO<sub>2</sub> interfaces, and controlled pore development.

The sp<sup>2</sup>-hybridised carbon framework of GR contains delocalised  $\pi$ -electron domains that can interact with the aromatic structure of MB through non-covalent  $\pi$ - $\pi$  association. Experimental studies involving pristine graphene and reduced graphene oxide have shown that MB uptake may arise from the combined contributions of aromatic interactions and charge-dependent attraction.<sup>88,89</sup> Hydrophobic affinity and dispersion forces may provide additional stabilisation when graphitic surfaces remain sufficiently exposed within the aqueous phase.<sup>90</sup> Graphitic materials may also contribute weak electrostatic and van der Waals interactions, depending on their surface condition and the chemistry of the surrounding aqueous phase. Within the hybrid membrane, these interactions may enhance MB retention when the GR sheets are uniformly distributed and remain accessible to the dye molecules. Conversely, excessive GR aggregation or sheet restacking may reduce the exposed graphitic surface area and conceal adsorption-active regions, thereby restricting MB access to available interaction sites.<sup>91</sup> Graphene-based adsorbents have been reported to enhance organic-pollutant uptake through

**Table 9** PSO kinetic model parameters for MB adsorption onto PVDF/NC/3% TiO<sub>2</sub> and GR-incorporated PVDF/NC/TiO<sub>2</sub> membranes at varying initial MB concentration and 25 °C

| Experiment 3: GR-incorporated membranes | Parameters                                                 | Initial MB concentration (ppm) |                       |                       |                       |                       |
|-----------------------------------------|------------------------------------------------------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                                         |                                                            | 1                              | 2                     | 3                     | 4                     | 5                     |
| PVDF/NC/3% TiO <sub>2</sub> (baseline)  | $q_e$ (mg m <sup>-2</sup> )                                | 485.04                         | 958.78                | 1441.61               | 1926.31               | 2408.14               |
|                                         | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.40 \times 10^{-4}$          | $1.39 \times 10^{-4}$ | $5.55 \times 10^{-5}$ | $6.14 \times 10^{-5}$ | $6.21 \times 10^{-5}$ |
|                                         | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.1% GR       | $q_e$ (mg m <sup>-2</sup> )                                | 488.71                         | 968.08                | 1454.50               | 1934.66               | 2414.23               |
|                                         | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.36 \times 10^{-4}$          | $1.38 \times 10^{-4}$ | $5.54 \times 10^{-5}$ | $6.54 \times 10^{-5}$ | $6.86 \times 10^{-5}$ |
|                                         | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.2% GR       | $q_e$ (mg m <sup>-2</sup> )                                | 493.42                         | 975.18                | 1466.01               | 1953.95               | 2442.68               |
|                                         | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.32 \times 10^{-4}$          | $1.37 \times 10^{-4}$ | $5.47 \times 10^{-5}$ | $6.71 \times 10^{-5}$ | $6.95 \times 10^{-5}$ |
|                                         | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.3% GR       | $q_e$ (mg m <sup>-2</sup> )                                | 479.27                         | 953.86                | 1434.37               | 1896.09               | 2357.32               |
|                                         | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.38 \times 10^{-4}$          | $1.40 \times 10^{-4}$ | $5.67 \times 10^{-5}$ | $6.75 \times 10^{-5}$ | $7.08 \times 10^{-5}$ |
|                                         | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.4% GR       | $q_e$ (mg m <sup>-2</sup> )                                | 434.45                         | 864.07                | 1299.76               | 1727.89               | 2153.59               |
|                                         | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.59 \times 10^{-4}$          | $1.55 \times 10^{-4}$ | $1.03 \times 10^{-4}$ | $7.74 \times 10^{-5}$ | $7.31 \times 10^{-5}$ |
|                                         | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.5% GR       | $q_e$ (mg m <sup>-2</sup> )                                | 389.63                         | 774.28                | 1165.15               | 1559.70               | 1949.87               |
|                                         | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.83 \times 10^{-4}$          | $1.73 \times 10^{-4}$ | $1.15 \times 10^{-4}$ | $7.57 \times 10^{-5}$ | $7.32 \times 10^{-5}$ |
|                                         | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |

combined  $\pi$ - $\pi$  interactions, hydrophobic association, hydrogen bonding, and electrostatic attraction.<sup>92</sup> Evidence from porous bionanocomposite adsorbents further demonstrates the importance of accessible internal interfaces. High dye adsorption by cellulose nanofibre/protein nanofibre/chitosan aerogel beads was attributed to accessible internal surfaces, controlled diffusion, and multiple intermolecular interactions.<sup>93</sup> MB adsorption onto activated carbon was similarly governed by the combined effects of surface area, pore volume, and pore-size distribution.<sup>94</sup> Collectively, these findings indicate that adsorption performance in hybrid membranes depends on the accessibility and spatial distribution of interaction domains rather than on pore size alone.

Further GR incorporation produced lower equilibrium capacities. At 5 ppm MB,  $q_e$  reached 2357.32, 2153.59, and 1949.87 mg m<sup>-2</sup> for the membranes containing 0.3%, 0.4%, and 0.5% GR, respectively. Increasing GR content promoted a greater tendency towards nanosheet restacking, aggregation, and partial masking of NC, TiO<sub>2</sub>, and graphitic adsorption regions.<sup>95</sup> At higher GR loadings, particularly 0.4% and 0.5%, FESEM analysis in the previous work showed a transition towards a coarser and more open membrane architecture, while the mean pore size increased from  $5.53 \times 10^{-3}$   $\mu$ m at 0.4% GR to  $12.56 \times 10^{-3}$   $\mu$ m at 0.5% GR.<sup>26</sup> These structural changes coincided with higher MB rejection flux but substantially lower MB removal efficiency, indicating that the enlarged and less controlled transport pathways facilitated dye passage and reduced the opportunity for MB retention at accessible interfacial domains. This behaviour is consistent with a shorter effective contact time between MB molecules and the membrane structure, although residence time was not measured directly. Enlargement of membrane pores can enhance permeation but may simultaneously compromise solute rejection by weakening size-based selectivity.<sup>96</sup>

Comparable permeability selectivity trade-offs have been reported for GR-containing PVDF membranes, in which increased pore openness facilitated water transport, whereas excessive structural enlargement reduced molecular sieving efficiency and dye retention.<sup>97</sup> The  $k_2$  values further demonstrate the importance of evaluating the rate constant together with equilibrium capacity. At 5 ppm MB, PVDF/NC/TiO<sub>2</sub>/0.2% GR achieved a  $q_e$  of 2442.68 mg m<sup>-2</sup> with a  $k_2$  of  $6.95 \times 10^{-5}$  m<sup>2</sup> mg<sup>-1</sup> min<sup>-1</sup>. The membranes containing 0.4% and 0.5% GR recorded lower  $q_e$  values of 2153.59 and 1949.87 mg m<sup>-2</sup>, despite  $k_2$  values of  $7.31 \times 10^{-5}$  and  $7.32 \times 10^{-5}$  m<sup>2</sup> mg<sup>-1</sup> min<sup>-1</sup>, respectively. These higher rate constants represent more rapid occupation of a smaller population of accessible adsorption sites rather than greater total MB uptake. PSO rate constants are condition-dependent and may yield incomplete or misleading kinetic interpretations when evaluated independently of the corresponding equilibrium adsorption capacity.<sup>98</sup> The GR series therefore reveals a distinct permeability-selectivity balance. Low GR loading enhanced MB adsorption by providing accessible graphitic interaction regions while preserving controlled membrane transport. Higher loading promoted restacking and greater pore openness, which reduced residence time and adsorption-assisted retention. Consequently, water transport and dye-removal performance require integrated evaluation in graphitic hybrid membranes.

**3.4.3 Effect of GO-mHM incorporation on MB adsorption and loading tolerance.** Following evaluation of the permeability-selectivity trade-off in GR-containing membranes, GO-mHM was introduced to determine whether its oxygen-rich surface chemistry could provide stronger MB interactions while maintaining performance across a broader loading range. Replacing GR with GO-mHM within the same PVDF/NC/3.0% TiO<sub>2</sub> framework also enabled direct comparison between graphitic and oxygenated graphene-derived fillers. Table 10

**Table 10** PSO kinetic model parameters for PVDF/NC/3% TiO<sub>2</sub> and GO-incorporated PVDF/NC/TiO<sub>2</sub> membranes at varying initial MB concentration and 25 °C

| Experiment 4: GO-mHM-incorporated membranes | Parameters                                                 | Initial MB concentration (ppm) |                       |                       |                       |                       |
|---------------------------------------------|------------------------------------------------------------|--------------------------------|-----------------------|-----------------------|-----------------------|-----------------------|
|                                             |                                                            | 1                              | 2                     | 3                     | 4                     | 5                     |
| PVDF/NC/3% TiO <sub>2</sub> (baseline)      | $q_e$ (mg m <sup>-2</sup> )                                | 485.04                         | 958.78                | 1441.61               | 1926.31               | 2408.14               |
|                                             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.40 \times 10^{-4}$          | $1.39 \times 10^{-4}$ | $9.31 \times 10^{-5}$ | $6.94 \times 10^{-5}$ | $5.55 \times 10^{-5}$ |
|                                             | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.1% GO-mHM       | $q_e$ (mg m <sup>-2</sup> )                                | 483.62                         | 968.39                | 1454.33               | 1941.43               | 2429.71               |
|                                             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.76 \times 10^{-4}$          | $1.38 \times 10^{-4}$ | $9.19 \times 10^{-5}$ | $6.89 \times 10^{-5}$ | $5.50 \times 10^{-5}$ |
|                                             | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.2% GO-mHM       | $q_e$ (mg m <sup>-2</sup> )                                | 487.89                         | 976.95                | 1467.19               | 1958.59               | 2451.18               |
|                                             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.74 \times 10^{-4}$          | $1.37 \times 10^{-4}$ | $9.11 \times 10^{-5}$ | $6.38 \times 10^{-5}$ | $5.45 \times 10^{-5}$ |
|                                             | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.3% GO-mHM       | $q_e$ (mg m <sup>-2</sup> )                                | 490.57                         | 982.33                | 1475.11               | 1967.70               | 2462.38               |
|                                             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.73 \times 10^{-4}$          | $1.36 \times 10^{-4}$ | $9.06 \times 10^{-5}$ | $6.79 \times 10^{-5}$ | $5.43 \times 10^{-5}$ |
|                                             | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.4% GO-mHM       | $q_e$ (mg m <sup>-2</sup> )                                | 480.38                         | 961.41                | 1443.85               | 1927.44               | 2412.19               |
|                                             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.78 \times 10^{-4}$          | $1.37 \times 10^{-4}$ | $9.13 \times 10^{-5}$ | $6.84 \times 10^{-5}$ | $5.47 \times 10^{-5}$ |
|                                             | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |
| PVDF/NC/TiO <sub>2</sub> /0.5% GO-mHM       | $q_e$ (mg m <sup>-2</sup> )                                | 455.28                         | 912.39                | 1371.32               | 1830.62               | 2291.03               |
|                                             | $k_2$ (m <sup>2</sup> mg <sup>-1</sup> min <sup>-1</sup> ) | $2.94 \times 10^{-4}$          | $1.47 \times 10^{-4}$ | $9.75 \times 10^{-5}$ | $7.30 \times 10^{-5}$ | $5.84 \times 10^{-5}$ |
|                                             | $R^2$                                                      | 0.98                           | 0.98                  | 0.98                  | 0.98                  | 0.98                  |

summarises the PSO kinetic parameters for the PVDF/NC/3.0% TiO<sub>2</sub> baseline and GO-mHM-incorporated PVDF/NC/TiO<sub>2</sub> membranes. The parameters define the effects of oxygenated graphene-derived filler loading on equilibrium capacity, apparent adsorption rate, and model-fitting consistency.

Based on the tabulated data at 5 ppm MB,  $q_e$  increased from 2408.14 mg m<sup>-2</sup> for PVDF/NC/3.0% TiO<sub>2</sub> to 2429.71, 2451.18, and 2462.38 mg m<sup>-2</sup> for membranes containing 0.1%, 0.2%, and 0.3% GO-mHM, respectively. The 0.3% GO-mHM formulation produced the highest equilibrium capacity within the series, while PSO  $R^2$  values remained approximately 0.98 throughout the investigated concentration range. Fig. 5 compares the PVDF/NC/3.0% TiO<sub>2</sub> baseline with membranes containing 0.1–0.5% GR and 0.1–0.5% GO-mHM. The comparison identifies optimal loadings of 0.2% GR and 0.3% GO-mHM and demonstrates greater retention of adsorption capacity in the GO-mHM series at elevated filler content.

The enhanced adsorption response of the GO-mHM-containing membranes in Fig. 5 is consistent with the greater abundance of oxygen-containing functionalities within the graphene-derived filler. These polar groups may improve interfacial compatibility with the NC/TiO<sub>2</sub>-containing matrix, promote more uniform filler distribution, and increase the accessibility of dye-interacting regions within the membrane structure. In aqueous media, oxygenated graphene surfaces can contribute to MB retention through charge-dependent attraction, hydrogen bonding, dipole interactions, and  $\pi$ - $\pi$  association between the residual graphitic domains and the aromatic structure of MB.<sup>45,99,100</sup> The relative contributions of these interactions depend primarily on the accessibility, dispersion, and interfacial exposure of the oxygenated graphene regions within the membrane matrix. Uniformly distributed GO-derived sheets can provide greater access to polar functional groups and residual graphitic domains. In contrast, aggregation or restacking may shield adsorption-active regions and restrict dye transport towards the filler surface.<sup>91,101</sup> Greater MB uptake by GO than by reduced graphene oxide has been attributed to its higher oxygen functional group density, larger accessible surface area, and stronger combined contributions from electrostatic attraction, hydrogen bonding, and  $\pi$ -related interactions.<sup>45</sup> Although this comparison was established using

dispersed graphene-based adsorbents, the reported dependence of MB affinity on surface oxygenation and accessible interfacial area provides relevant mechanistic support for the loading-dependent behaviour of the GO-mHM-containing membranes.

The EDX analysis provided complementary compositional evidence for the persistence of oxygen-rich regions across the GO-mHM membrane series, with oxygen contents ranging from 41.83 to 43.19 wt%. Although EDX does not distinguish individual oxygen-containing functional groups, the consistently high oxygen signal, when interpreted together with the FTIR results, supports the retention of oxygen-bearing GO-mHM-related species after membrane fabrication. At low to moderate GO-mHM loadings, these oxygen-rich regions likely increased membrane polarity and strengthened filler-matrix compatibility, consistent with the improved MB adsorption observed at 0.3% GO-mHM. Comparable behaviour has been reported for GO-modified carbon nanotube buckypaper membranes, where strong adsorption of cationic dyes was associated with favourable interactions between the dye molecules and negatively charged GO-containing surfaces.<sup>30</sup> At higher GO-mHM loading, the equilibrium capacity reached 2412.19 and 2291.03 mg m<sup>-2</sup> for the 0.4% and 0.5% formulations, respectively. This downturn suggests that further filler addition reduced the accessibility of adsorption-active regions through nanosheet association and partial restacking, consistent with van der Waals and  $\pi$ - $\pi$ -driven aggregation reported for GO-based materials.<sup>102</sup>

High-shear homogenisation during membrane preparation was employed to facilitate GO-mHM dispersion throughout the casting solution. Comparable processing has been shown to improve GO distribution within PVDF matrices, thereby enhancing membrane hydrophilicity, water permeability, and pollutant rejection.<sup>50</sup> Nevertheless, the decline in  $q_e$  at 0.4% and 0.5% GO-mHM indicates that homogenisation did not fully prevent loading-induced nanosheet association above the optimum loading. At these higher loadings, partial agglomeration and restacking likely reduced the exposure of adsorption-active regions and disrupted favourable pore development, thereby limiting the contribution of additional GO-mHM to MB uptake. This interpretation is consistent with previous findings showing that the performance of GO-containing polymeric membranes is governed not only by GO loading, but also by the degree of filler dispersion, interfacial compatibility, and spatial distribution throughout the polymer matrix.<sup>103</sup> The adsorption penalty beyond the optimum loading was less pronounced for GO-mHM than for GR. At a filler loading of 0.5%, the GO-mHM membrane retained a  $q_e$  of 2291.03 mg m<sup>-2</sup>, whereas the corresponding GR-containing membrane exhibited a lower value of 1949.87 mg m<sup>-2</sup>. This difference indicates that GO-mHM was more tolerant to elevated loading within the PVDF/NC/TiO<sub>2</sub> matrix. The greater retention of adsorption capacity may be associated with the higher density of oxygen-containing functionalities in GO, which can strengthen filler-matrix interactions and preserve a larger fraction of accessible dye-interacting regions despite partial nanosheet association. Higher MB uptake by GO-modified adsorbents than by reduced-GO

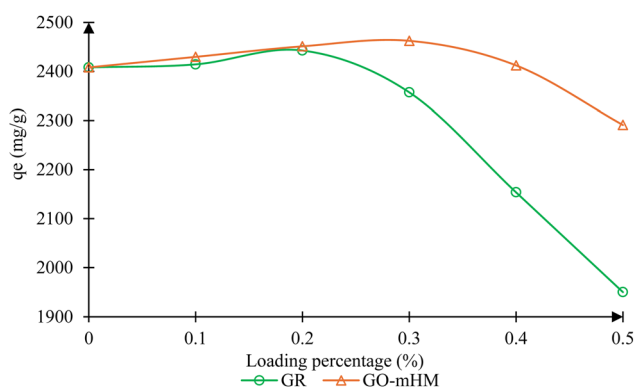


Fig. 5 Loading-dependent MB adsorption performance of GR- and GO-mHM-incorporated membranes.

analogues has similarly been attributed to the greater abundance of oxygen-containing surface functionalities.<sup>104</sup>

The relationship between  $q_e$  and  $k_2$  followed the same general pattern observed for the GR-containing membranes. At 5 ppm MB, the 0.3% GO-mHM membrane achieved the highest  $q_e$  of 2462.38 mg m<sup>-2</sup>, with a  $k_2$  value of  $5.43 \times 10^{-5}$  m<sup>2</sup> mg<sup>-1</sup> min<sup>-1</sup>. By comparison, the 0.5% membrane exhibited a slightly higher  $k_2$  of  $5.84 \times 10^{-5}$  m<sup>2</sup> mg<sup>-1</sup> min<sup>-1</sup> but a lower  $q_e$  of 2291.03 mg m<sup>-2</sup>. Although the 0.5% GO-mHM membrane exhibited a marginally higher  $k_2$ , its nearly identical  $k_2 q_e$  value and lower equilibrium capacity indicate that MB uptake did not occur appreciably faster than in the 0.3% formulation. The higher  $k_2$  should therefore not be interpreted independently as evidence of superior adsorption performance, because its kinetic meaning remains coupled to the corresponding  $q_e$ . The initial adsorption rate,  $h = k_2 q_e^2$ , provides a more integrated comparison by accounting for both apparent rate and equilibrium capacity. At 5 ppm MB, the 0.3% GO-mHM membrane exhibited an  $h$  value of 329.24 mg m<sup>-2</sup> min<sup>-1</sup>, exceeding the 306.53 mg m<sup>-2</sup> min<sup>-1</sup> obtained for the 0.5% formulation. This result confirms that the 0.3% membrane achieved the most favourable overall kinetic response by combining high adsorption capacity with a rapid initial uptake rate. Such behaviour is consistent with the combined influence of concentration-driven mass transfer, accessible adsorption regions, and effective nanofiller integration on the apparent adsorption response.<sup>53,105</sup>

### 3.5 Comparative equilibrium adsorption behaviour of TiO<sub>2</sub>, GR, and GO-mHM-modified hybrid membranes

The equilibrium behaviour of the TiO<sub>2</sub>, GR, and GO-mHM-incorporated membranes was evaluated using the Freundlich models. Table 11 summarises the Freundlich  $K_F$ ,  $1/n$ , and  $R^2$  values. These parameters enable comparison of heterogeneous adsorption affinity ( $K_F$ ) and apparent adsorption capacity ( $q_{\max}$ ) across the membrane formulations developed in Experiments 2, 3, and 4. The corresponding Freundlich plots are compiled in Table 12, providing a visual comparison of the regression behaviour across the three-membrane series.

The Freundlich model provided the most consistent and physically meaningful representation of the equilibrium data, with  $R^2$  values predominantly ranging from 0.97 to 0.99. The nonlinear fitted curves presented in Table 12 further demonstrate the consistently strong agreement between the Freundlich model predictions and the experimental equilibrium adsorption data across the TiO<sub>2</sub>, GR, and GO mHM modified membranes. Within the TiO<sub>2</sub> series, the Freundlich constant ( $K_F$ ) increased from 2232.03 for PVDF-4% NCM to 19 843.16 for PVDF/NC/3.0% TiO<sub>2</sub>. At higher TiO<sub>2</sub> loadings,  $K_F$  declined to 6457.83 and 2452.40 for the 3.5% and 4.0% formulations, respectively.

For the GR-containing membranes, both models identified PVDF/NC/TiO<sub>2</sub>/0.2% GR as the optimum formulation. The  $K_F$  value increased from 19 843.16 for the TiO<sub>2</sub>-containing baseline to 31 132.00 after incorporating 0.2% GR. Further increases in GR loading reduced  $K_F$  to 8074.68, 2987.04, and 1593.22 for the 0.3%, 0.4%, and 0.5% formulations, respectively. At this

**Table 11** Freundlich isotherm parameters obtained by nonlinear regression for membranes developed in Experiments 2, 3 and 4 at 25 °C

| Membranes                                                   | Freundlich                                                       |       |       |
|-------------------------------------------------------------|------------------------------------------------------------------|-------|-------|
|                                                             | $K_F$ (mg m <sup>-2</sup> ) (L mg <sup>-1</sup> ) <sup>1/n</sup> | $1/n$ | $R^2$ |
| <b>Experiment 2: TiO<sub>2</sub>-incorporated membranes</b> |                                                                  |       |       |
| PVDF-4% NCM                                                 | 2232.03                                                          | 0.911 | 0.99  |
| PVDF/NC/2% TiO <sub>2</sub>                                 | 3308.50                                                          | 0.84  | 0.99  |
| PVDF/NC/2.5% TiO <sub>2</sub>                               | 4795.21                                                          | 0.84  | 0.99  |
| PVDF/NC/3% TiO <sub>2</sub>                                 | 19 843.16                                                        | 0.83  | 0.99  |
| PVDF/NC/3.5% TiO <sub>2</sub>                               | 6457.83                                                          | 0.94  | 0.96  |
| PVDF/NC/4% TiO <sub>2</sub>                                 | 2452.40                                                          | 0.84  | 0.99  |
| <b>Experiment 3: GR-incorporated membranes</b>              |                                                                  |       |       |
| PVDF/NC/3% TiO <sub>2</sub>                                 | 19 843.16                                                        | 0.83  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.1% GR                           | 16 843.54                                                        | 0.98  | 0.98  |
| PVDF/NC/TiO <sub>2</sub> /0.2% GR                           | 31 132.00                                                        | 0.91  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.3% GR                           | 8074.68                                                          | 0.98  | 0.97  |
| PVDF/NC/TiO <sub>2</sub> /0.4% GR                           | 2987.04                                                          | 0.96  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.5% GR                           | 1593.22                                                          | 0.95  | 0.99  |
| <b>Experiment 4: GO-mHM-incorporated membranes</b>          |                                                                  |       |       |
| PVDF/NC/3% TiO <sub>2</sub>                                 | 19 843.16                                                        | 0.83  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.1% GO-mHM                       | 27 396.18                                                        | 0.87  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.2% GO-mHM                       | 42 205.06                                                        | 0.88  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.3% GO-mHM                       | 75 501.71                                                        | 0.85  | 0.99  |
| PVDF/NC/TiO <sub>2</sub> /0.4% GO-mHM                       | 18 668.91                                                        | 0.90  | 0.97  |
| PVDF/NC/TiO <sub>2</sub> /0.5% GO-mHM                       | 5351.91                                                          | 0.96  | 0.99  |

concentration, effective GR dispersion likely preserved accessible graphitic regions, thereby strengthening MB affinity and increasing the apparent adsorption capacity. Similar loading-dependent improvements have been reported for other graphene-containing adsorbents. For example, graphene incorporation into porous carbon foam increased MB adsorption by approximately 93.5%, primarily through improved pore development and greater adsorption-site availability.<sup>106</sup> Similarly, adding only 1 wt% rGO to a geopolymer increased the Langmuir maximum capacity from 13.2 to 22.7 mg g<sup>-1</sup>.<sup>106</sup> These findings indicate that modest GR-based additions can enhance adsorption when effective dispersion and matrix integration preserve accessible adsorption regions.

In contrast, the GO-mHM series exhibited a pronounced non-monotonic loading response, with the most favourable equilibrium adsorption behaviour obtained at 0.3% GO-mHM. The Freundlich  $K_F$  increased from 19 843.16 for the baseline membrane to 27 396.18, 42 205.06, and 75 501.71 at 0.1%, 0.2%, and 0.3% GO-mHM, respectively. However, further loading caused  $K_F$  to decline sharply to 18 668.91 at 0.4% and 5351.91 at 0.5% GO-mHM. This reduction indicates that excessive GO-mHM loading diminished the apparent adsorption affinity of the heterogeneous membrane domains. The progressive increase in Freundlich  $K_F$  across the optimum membrane sequence indicates that sequential nanofiller incorporation enhanced the apparent affinity of the heterogeneous adsorption domains. The highest  $K_F$  obtained for PVDF/NC/TiO<sub>2</sub>/0.3% GO-mHM, suggests that oxygen-containing functional groups in GO-mHM made an important contribution to MB adsorption.

**Table 12** Comparison of nonlinear Freundlich isotherm fitting for MB adsorption onto membranes developed in Experiments 2, 3 and 4 at 25 °C

| Experiment                                             | Freundlich model |
|--------------------------------------------------------|------------------|
| Experiment 2: TiO <sub>2</sub> -incorporated membranes |                  |
| Experiment 3: GR-incorporated membranes                |                  |
| Experiment 4: GO-mHM-incorporated membranes            |                  |

GO-mHM also retained stronger equilibrium adsorption parameters than GR at elevated loading. At 0.4% loading, the GO-mHM membrane exhibited a  $K_F$  of 18 668.91, whereas the corresponding GR membrane produced substantially lower values of 2987.04 and 2523.80  $\text{mg m}^{-2}$ , respectively. This difference suggests that the oxygen-containing functionalities of GO-mHM promoted more favourable interfacial integration with NC and TiO<sub>2</sub>, thereby preserving a larger fraction of accessible adsorption domains within the PVDF matrix. Similar behaviour has been reported for nanocellulose-based hybrid systems incorporating hydrophilic additives or graphene oxide, although excessive filler loading can still promote agglomeration, structural non-uniformity, and reduced accessibility of functional domains.<sup>89,107</sup>

The progressive increase in Freundlich  $K_F$  across the optimum formulation sequence indicates that sequential incorporation of NC, TiO<sub>2</sub>, GR, and GO-mHM enhanced the apparent affinity of the heterogeneous adsorption domains. The maximum  $K_F$  obtained for PVDF/NC/TiO<sub>2</sub>/0.3% GO-mHM supports a substantial contribution from oxygen-containing graphene-derived regions to MB uptake. Because the Freundlich exponent varied only narrowly across the membrane series, comparison of  $K_F$  within the common concentration range provides a reasonable

indication of relative adsorption affinity. On the other hand, GO-mHM also preserved more favourable equilibrium adsorption characteristics than GR at an equivalent elevated loading. At 0.4% filler content, the GO-mHM membrane exhibited a  $K_F$  of 18 668.91, whereas the corresponding GR membrane produced substantially lower values of 2987.04 and 2523.80  $\text{mg m}^{-2}$ , respectively. This contrast is consistent with the oxygen-containing functionalities of GO-mHM promoting more favourable interfacial integration with NC and TiO<sub>2</sub>, thereby maintaining greater accessibility to adsorption active regions within the PVDF matrix. The adsorption trends are consistent with more effective integration of GO-mHM within the NC/TiO<sub>2</sub>/PVDF matrix as further supported by the corresponding morphological and chemical characterisation.

### 3.6 Integrated mechanistic interpretation of adsorption kinetics, equilibrium behaviour and membrane characteristics

The use of area specific adsorption capacity is particularly relevant to this coupled membrane system because it relates MB uptake to the same active membrane geometry through which permeation and solute retention occur. Additionally, the adsorption results provide an evidence based mechanistic

interpretation of MB uptake rather than direct identification of individual molecular adsorption pathways. The PSO model provided the most consistent kinetic representation across the membrane series, whereas the Freundlich model gave the most physically coherent description of equilibrium adsorption. Most importantly, the PSO response is interpreted as an empirical representation of capacity dependent uptake and progressive occupation of accessible adsorption regions rather than as direct evidence of a particular chemical bonding mechanism. Similarly, the favourable Freundlich response supports adsorption within energetically heterogeneous membrane environments but does not independently identify the molecular interactions responsible for MB retention. The observed adsorption trends can nevertheless be interpreted in conjunction with the sequential membrane composition and available physicochemical characterisation. Incorporation of NC introduced hydroxyl rich domains, while  $\text{TiO}_2$  provided polar inorganic interfaces and GR introduced graphitic domains capable of interacting with the aromatic structure of MB. GO-mHM further introduced oxygen bearing graphene derived regions. For the GO-mHM membrane series, EDX showed oxygen contents of 41.83 to 43.19 wt%, and the oxygen signal interpreted together with the FTIR observations supports the persistence of oxygen bearing species following membrane fabrication. These compositional features provide a reasonable physicochemical basis for the enhanced MB affinity observed after sequential membrane modification, although they do not independently demonstrate the contribution of a specific

adsorption interaction. Loading dependent behaviour provides additional evidence for the importance of interfacial accessibility. Each filler displayed an optimum concentration rather than a monotonic improvement with increasing loading. The optimum formulations were PVDF 4% NCM, PVDF/NC/3.0%  $\text{TiO}_2$ , PVDF/NC/ $\text{TiO}_2$ /0.2% GR and PVDF/NC/ $\text{TiO}_2$ /0.3% GO-mHM. Beyond these loading levels, adsorption capacity decreased despite the greater nominal filler content.

For the GR series, the reduction corresponded with previously observed changes towards a coarser and more open membrane architecture at elevated GR loading, while the GO-mHM series similarly showed declining adsorption above 0.3% loading. These trends are consistent with particle aggregation, nanosheet restacking, partial masking of functional regions and altered pore development reducing the fraction of interfaces accessible to MB. The stronger adsorption response of GO-mHM relative to GR is also consistent with differences in filler chemistry. Oxygenated graphene surfaces may participate in electrostatic attraction, hydrogen bonding and dipole interactions, while residual graphitic domains can support  $\pi$ - $\pi$  association with aromatic MB molecules. Graphitic regions in GR may similarly contribute to  $\pi$ - $\pi$  interactions. However, the present kinetic, equilibrium and characterisation data do not permit quantitative separation of electrostatic, hydrogen bonding,  $\pi$ - $\pi$ , van der Waals and pore associated contributions. Overall, the combined evidence indicates that the progressive adsorption enhancement is consistent with the development of chemically heterogeneous and increasingly

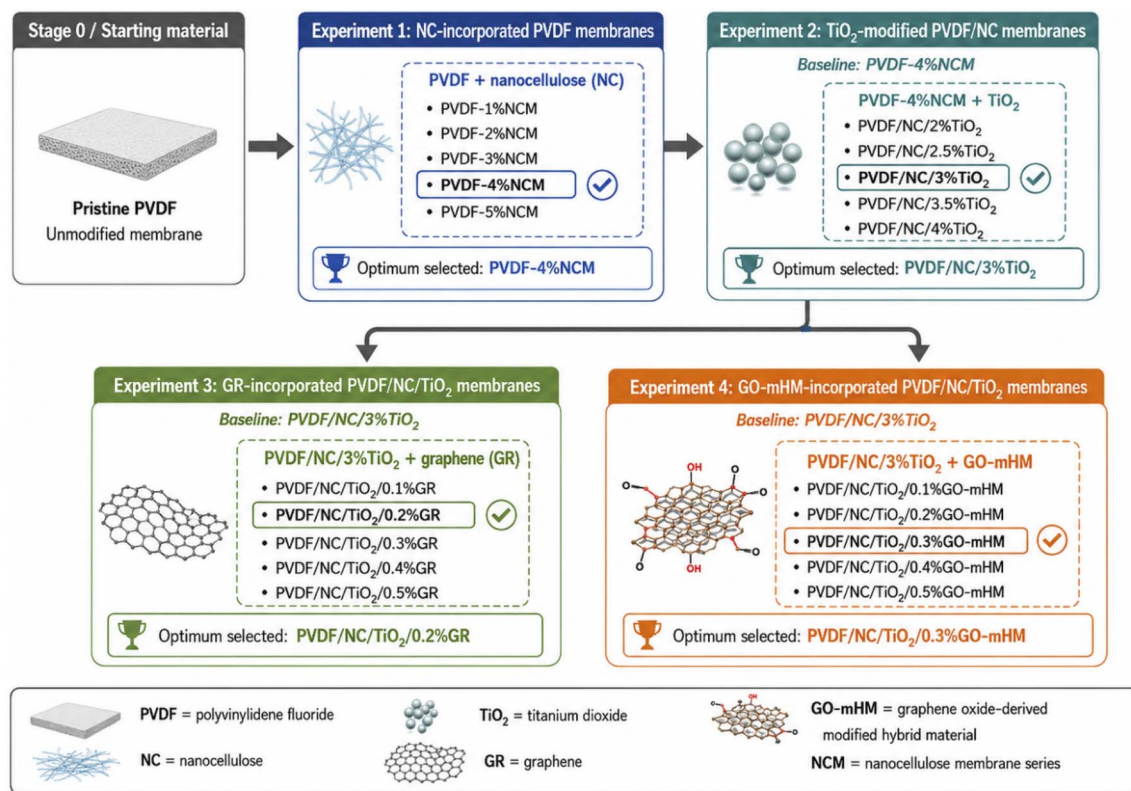


Fig. 6 Sequential modification pathway and nomenclature of PVDF/NC/ $\text{TiO}_2$ /carbon based hybrid membranes investigated for adsorption-separation coupling during methylene blue removal.

accessible interfacial regions within the modified PVDF membranes, as shown by Fig. 6.

### 3.7 Conclusion

This study established the influence of the sequential incorporation of NC, TiO<sub>2</sub>, GR, and GO-mHM on MB adsorption across the entire PVDF hybrid membrane series. The equilibrium capacity increased from 1049.79 mg m<sup>-2</sup> for pristine PVDF to 2462.38 mg m<sup>-2</sup> for PVDF/NC/TiO<sub>2</sub>/0.3% GO-mHM. This confirmed the progressive contribution of each modification stage within a distinct optimum loading range. The PSO model provided the most consistent kinetic representation, while the Freundlich model indicated heterogeneous equilibrium adsorption. Adsorption response declined beyond the optimum loading, which is consistent with increased filler association, nanosheet restacking and reduced accessibility of interfacial adsorption regions. Overall, the kinetic, equilibrium and loading dependent trends, interpreted together with the available membrane characterisation, indicate that filler chemistry, dispersion, heterogeneous interfacial environments and adsorption site accessibility influenced MB uptake.

## Author contributions

Anthonette James: writing – original draft, review & editing methodology, conceptualization, investigation., Md Rezaur Rahmana, Ervina binti Junaidi, Calvin Jose Jol, and Murtala Namakka: writing – original draft, visualization, software, methodology, investigation, formal analysis, data curation.

## Conflicts of interest

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

## Data availability

All the data in this study are included within this article.

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