

Comparative evaluation of ion-exchange resins for natural organic matter removal from power plant source waters

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ABSTRACT

Natural organic matter (NOM) in source waters presents significant operational challenges for thermal power generation, including membrane fouling, scaling, and the formation of disinfection byproducts (DBPs). This study evaluated the performance of three macroporous strong-base anion exchange (IEX) resins, polyacrylic (A860S), polystyrenic (A502PS), and a polystyrene-polyacrylic blend (MPR1000), for dissolved organic carbon (DOC) removal from two industrial water sources: Vaal River raw water (Vaal RW) and Medupi ultrafiltrate (Medupi UF). Batch experiments and kinetic modelling revealed that the pseudo-second-order model best described the adsorption behaviour, indicating chemisorption as the dominant removal mechanism. Despite having the lowest ion-exchange capacity, MPR1000 achieved the highest DOC uptake in Medupi UF ($47.4 \pm 3.2\%$), while A860S demonstrated the most consistent performance across both matrices (up to $77.3 \pm 4.2\%$ in Vaal RW). In contrast, A502PS exhibited limited effectiveness due to diffusional constraints. Intraparticle diffusion analysis confirmed multi-stage mass transfer, and liquid chromatography-organic carbon detection showed preferential removal of humic substances and building blocks, with minimal uptake of low molecular weight acids and neutrals. Variations in removal efficiency were attributed not to the molecular weight of NOM but to differences in aromaticity ($SUVA_{254}$) and anionic composition, particularly the sulphate content. These findings underscore the importance of aligning resin matrix characteristics with specific water chemistries to optimise IEX performance for industrial water treatment, particularly under sulphate-rich conditions common in power plant operations.

1. Introduction

Natural organic matter (NOM) is a heterogeneous mixture of organic compounds originating from the decomposition of plant and microbial material. Its presence in source waters poses both operational and regulatory challenges in drinking water treatment and industrial applications such as thermal power generation [1,2]. NOM increases coagulant and disinfectant demand, impairs membrane and ion exchange performance, and serves as a precursor for carcinogenic disinfection byproducts (DBPs), which are subject to strict regulatory limits [3–7]. In high-temperature power plant systems, NOM can decompose to low molecular weight acids that accelerate corrosion and scaling, thereby reducing system performance and lifespan [8–12].

A broad spectrum of treatment technologies have been developed to address this challenge, including coagulation-flocculation, membranes, adsorption, advanced oxidation processes, and biological treatments

[13]. Among these, anion exchange (IEX) has emerged as a promising approach due to its ability to selectively remove negatively charged NOM fractions, particularly carboxylated and phenolic moieties [14, 15]. IEX is increasingly evaluated as a flexible treatment option where coagulation and activated carbon show limited effectiveness, especially for hydrophilic and low molecular weight fractions [16,17]. In power plant water treatment systems, IEX is commonly integrated as a pre-treatment step before demineralisation, thereby enhancing the removal of organic and inorganic contaminants [8,18]. However, IEX performance can be hindered by competing anions and organic fouling, especially in fixed-bed configurations and when treating high molecular weight or hydrophobic NOM fractions [19,20].

The efficiency of IEX is influenced by NOM characteristics (aromaticity, molecular size, charge density) and resin properties (polymer matrix, pore structure, functional group chemistry) [21–23]. Low

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Table 1

Physicochemical properties of macroporous strong-base anion exchange resins functionalised with quaternary ammonium groups (manufacturer-provided). Key differences include polymer matrix composition, water content, and ion exchange capacity, all of which influence adsorption behaviour.

Resin	Matrix	Functional group	Particle size (μm)	Water content (%)	Capacity (eq L^{-1})
A860S	Macroporous, polyacrylic	Quaternary ammonium	425–1200	66–72	0.80
A502PS	Macroporous, polystyrene	Quaternary ammonium	425–1200	70–75	0.85
MPR1000	Macroporous, polystyrene/acrylic	Quaternary ammonium	425–1200	68–74	0.65

molecular weight, highly charged fractions are more readily removed due to enhanced diffusion and stronger electrostatic interactions with resin functional groups. Polyacrylic resins offer faster kinetics due to their hydrophilic, swollen structure, while polystyrenic resins provide greater chemical stability but often slower mass transfer [24,25]. Comparative studies have reported variable NOM removal performance across resin types [26,27]. Macroporous strong-base anion resins functionalised with quaternary ammonium groups in chloride form are commonly employed for NOM removal due to improved accessibility to exchange sites [7,28].

Detailed characterisation of NOM is essential for mechanistic interpretation of removal behaviour and optimisation of treatment performance. Techniques such as liquid chromatography-organic carbon detection (LC-OCD), high-performance size exclusion chromatography (HPSEC), and fluorescence spectroscopy allow for the identification and quantification of NOM fractions based on molecular size, polarity, and reactivity [29,30]. The framework of Huber et al. [31], which classifies NOM into biopolymers, humic substances, building blocks, low molecular weight (LMW) acids, and LMW neutrals, is widely adopted. This framework facilitates the mechanistic interpretation of NOM removal behaviours and informs the selection and design of targeted treatment technologies. Recent advances have also explored bicarbonate-form and biological IEX resins to reduce regeneration frequency and improve NOM removal sustainability. However, their application in industrial settings such as power generation remains limited [16].

This study systematically investigated the performance of three macroporous strong base anion exchange resins, polystyrenic, polyacrylic, and a mixed polystyrene–polyacrylic type, for NOM removal from surface water and ultrafiltration permeate intended for power generation. These water matrices represent partially treated and raw water scenarios where NOM composition and inorganic ion content vary significantly. Comprehensive NOM characterisation was conducted using dissolved organic carbon (DOC), specific ultraviolet absorbance (SUVA), and LC-OCD. Additionally, kinetic studies and surrogate compound removal experiments were used to elucidate removal mechanisms and assess the influence of NOM properties and resin characteristics. The findings provide valuable insights into the suitability of different resin types for NOM removal across diverse water qualities and inform the development of robust, resin-based pre-treatment strategies for thermal power plant applications.

2. Materials and methods

2.1. Ion exchange resins

Three commercial macroporous strong base anion exchange resins, Purolite A860S, A502PS, and MPR1000, were procured from Purolite (Pinetown, South Africa). All resins possessed quaternary ammonium functional groups and featured particle sizes ranging from 425 to 1200 μm . Their primary distinction was the polymeric backbone composition: acrylic, polystyrenic, or a hybrid of both. Detailed physicochemical characteristics of the resins, as provided by the manufacturer, are summarised in Table 1.

2.2. Sampling and water characterisation

Water samples were collected from two South African thermal power stations at distinct stages of the treatment process. Raw water (RW) was sourced from the Vaal River, which supplies the Lethabo Power Station in the Free State Province ($26^{\circ}43'47.7''\text{S}$, $28^{\circ}00'25.9''\text{E}$), while partially treated water was obtained post-ultrafiltration (UF) from Medupi Power Station in Limpopo Province, which uses water from the Mokolo River ($23^{\circ}40'33.2''\text{S}$, $27^{\circ}14'13.9''\text{E}$). All samples were collected in pre-cleaned 5 L polyethylene containers and rinsed thrice with site water to minimise contamination. Samples were transported on ice and stored at 4°C prior to analysis at Eskom's Research, Testing, and Development (RT&D) laboratory in Johannesburg, South Africa.

Before analysis, samples were filtered through $0.45\ \mu\text{m}$ PES membrane filters (Sartorius, Germany) to remove suspended solids. Dissolved organic carbon (DOC) concentrations were measured using a Sievers 900 TOC analyser (Chemetrix, South Africa), calibrated using potassium hydrogen phthalate standards across a $0\text{--}20\ \text{mg L}^{-1}$ range. A $5\ \text{mg L}^{-1}$ working standard served as a quality control check. All DOC analyses were performed in triplicate, with standard deviation maintained below 5%. In addition to descriptive statistics, one-way analysis of variance (ANOVA) was applied to assess the statistical significance of differences in resin performance and kinetic model fits. The significance threshold was set at $p < 0.05$.

Ultraviolet absorbance at 254 nm (UVA_{254}) was determined using a Jenway UV/Vis spectrophotometer (Genesys 10UV, Thermo Fisher Scientific, South Africa) and 1 cm quartz cuvettes. Ultra-pure water served as the blank. Specific ultraviolet absorbance (SUVA) was computed as the ratio of $\text{UVA}_{254}\ (\text{m}^{-1})$ to DOC (mg L^{-1}). Molecular characterisation of DOC was conducted via liquid chromatography with organic carbon detection (LC-OCD), following the method of Huber et al. [31]: separation was achieved using a polymethacrylate-based weak cation exchange column (TSK HW50S, $250\ \text{mm} \times 20\ \text{mm}$; Toso, Japan), with a phosphate buffer (pH 6.85) as the mobile phase. The buffer consisted of $2.5\ \text{g L}^{-1}$ potassium hydrogen phosphate and $1.5\ \text{g L}^{-1}$ sodium hydrogen phosphate, delivered at $1.1\ \text{mL min}^{-1}$. A 1 mL injection volume was used for each run.

Eluted fractions were first detected using a UV detector at 254 nm (Knauer S-200, Berlin, Germany). The effluent was subsequently acidified and passed through the organic carbon detector (OCD). Bespoke software (ChromCALC DOC-Labor, Karlsruhe, Germany) was employed for data acquisition and identification of DOC peaks according to Huber et al. [31]. In short: Organic carbon was separated into 5 different fractions: (i) biopolymers (peak 1 (P1), high molecular weight, e.g. extracellular polymers); (ii) humic substances (peak 2 (P2), medium molecular weight, increased SUVA); (iii) building blocks (P3, breakdown products of humic substances with lower molecular weight, highly variable SUVA); (iv) low molecular weight (LMW) acids (peak 4 (P4), anionic); and (v) low molecular weight neutrals (peak 5 (P5); hydro- or amphiphilic, low SUVA).

A $0.1\ \text{mL min}^{-1}$ bypass flow was used to determine total DOC for each run. The OCD and UV detectors were calibrated with potassium hydrogen phthalate; organic nitrogen detector (OND) calibration was

Table 2

Key physicochemical characteristics of Medupi ultrafiltrate (UF) and Vaal River raw water (RW), including pH, turbidity, TOC, hardness (CaCO_3), DOC, SUVA_{254} , sulphate, chloride, and total anions. DOC and SUVA_{254} (derived from LC-OCD analysis) reflect the specific experimental batches. These parameters define the contrasting water matrices used to evaluate resin performance.

Source water	pH (25 °C)	Turbidity (NTU)	TOC (mg L^{-1})	Hardness (mg L^{-1} as CaCO_3)	^a DOC (mg L^{-1})	^b SUVA ($\text{L mg}^{-1} \text{ m}^{-1}$)	Sulphate (mg L^{-1})	Anions (meq L^{-1})	Chloride (mg L^{-1})
Medupi UF	8.5	1.5	4.3	80	5.3 ± 0.3	2.03	172	5.45	30.6
Vaal RW	7.8	84.1	5.2	58	4.4 ± 0.3	3.08	13	1.55	5.4

^a DOC obtained from water used in experiments.

^b LC-OCD measurements based on chromatographable DOC.

conducted using potassium nitrate. For quantification of organic nitrogen, a fraction of the flow (0.1 mL min^{-1}) after the UV detector was diverted to the OND.

2.3. Batch ion exchange experiments

Batch adsorption experiments were performed using 0.4 g of resin in 200 mL of Medupi UF and 1.0 g in 200 mL of Vaal RW. The mixtures were agitated at 200 rpm on an orbital shaker (Stuart, UK) under ambient conditions, with contact times ranging from 5 to 240 min to assess temporal adsorption dynamics. After agitation, samples were allowed to settle for 2 min, and the supernatant was decanted for analysis. All adsorption experiments were conducted at the inherent pH of the source waters to reflect realistic operational conditions; systematic pH optimisation was beyond the scope of this study.

2.4. Kinetic modelling

To elucidate the adsorption kinetics of NOM onto the resins, three models were applied: pseudo-first-order (PFO), pseudo-second-order (PSO), and intra-particle diffusion (IPD). The PFO model assumes that the rate of solute uptake is proportional to the number of unoccupied adsorption sites and is represented by Eq. (1) [32].

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

Where q_t and q_e (mg g^{-1}) are the adsorption capacities at equilibrium and time t , respectively, and k_1 (min^{-1}) is the rate constant. The PSO model, assuming chemisorption as the rate-limiting step, is expressed by Eq. (2).

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

Where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the second-order rate constant. This model better describes systems where adsorption is governed by available active sites [32,33]. Intra-particle diffusion was analysed using the Weber–Morris model (Eq. (3)).

$$q_t = k_{id} t^{1/2} + C \quad (3)$$

Where k_{id} ($\text{mg g}^{-1} \text{ min}^{-0.5}$) is the intra-particle diffusion rate constant, and C (mg g^{-1}) indicates the boundary layer thickness (BLT). A linear plot of q_t versus $t^{1/2}$ passing through the origin suggests that intra-particle diffusion is the sole rate-limiting mechanism [34].

3. Results and discussion

3.1. Water sample characterisation

The physicochemical parameters of the Medupi UF and Vaal RW are presented in Table 2. These characteristics, alongside two-year historical TOC averages, serve as a foundational basis for assessing the comparative performance of the ion-exchange resins. The TOC values, sulphate concentrations, and ionic strengths varied considerably between the two water sources, which were critical in shaping the observed ion-exchange behaviours.

3.2. DOC removal efficiency from raw and treated waters

Fig. 1 depicts the time-resolved DOC removal profiles for Medupi UF and Vaal RW during treatment with three commercial macroporous strong base anion-exchange resins. In Medupi UF, all three resins demonstrated a two-phase kinetic behaviour, characterised by an initial rapid adsorption phase followed by a slower equilibrium phase reached within 120 min (Fig. 1a). Among the tested resins, MPR1000, comprising a mixed polystyrene-polyacrylic matrix, achieved the highest equilibrium DOC removal efficiency ($47.4 \pm 3.2\%$). The polyacrylic A860S and polystyrene A502PS resins showed limited removal efficiency, achieving maximum reductions of $34.3 \pm 1.6\%$ and $35.0 \pm 2.7\%$, respectively. These findings align with observations by Tran et al. [26], who reported comparable performance trends (A860: 25%–37% removal; A502PS: 15%–25% removal) in low-hydrophobicity feed waters.

In stark contrast, Vaal RW treatment demonstrated markedly faster DOC removal kinetics (Fig. 1b). Within the first 5 min, DOC removal efficiencies reached $25.8 \pm 1.5\%$, $47.7 \pm 3.7\%$, and $61.6 \pm 2.6\%$ for A502PS, MPR1000, and A860S, respectively. Equilibrium was generally attained between 30 and 60 min. Final DOC reductions ranged from $46.2 \pm 3.4\%$ (A502PS) to $77.3 \pm 4.2\%$ (A860S), underscoring significant performance enhancement relative to the Medupi UF matrix. The contrasting behaviours observed between the two water matrices emphasise the role of resin physicochemical structure and water quality.

3.3. Kinetic modelling of NOM removal

The adsorption kinetics of NOM removal from Medupi UF and Vaal RW were evaluated for the three IEX resins using PFO, PSO, and IPD models (Figs. 2, 3; Tables 3 and 4). The PSO model showed superior fits across most resin–matrix combinations, with adjusted $R^2 \geq 0.97$ and lower residual sum-of-squares (RSS) values than PFO (Table 3), supporting a chemisorption mechanism involving electrostatic and ion-exchange interactions between NOM functional groups and the resin's anionic sites and quaternary ammonium functionalities. The polymer architecture of polystyrenic resin exhibits inherent hydrophobicity, contrasting with the hydrophilic nature of polyacrylic resins [26,28]. This polarity difference critically influences their affinity for aqueous-phase organic compounds and contributes to the observed kinetic behaviour. Hence, an exception is noted for A520PS (UF and RW), where PFO is superior (Adj. $R^2 > 0.97$), suggesting a possible predominance of physisorption or rapid surface binding in these systems.

While PFO provided satisfactory fits for A502PS, it performed poorly for MPR1000 ($0.91 < \text{Adj. } R^2 < 0.94$) (Fig. 2a and Table 3). For A860S, both the PFO and PSO models yielded satisfactory fits in Medupi UF and Vaal RW, with adjusted R^2 values of 0.973 and 0.980 in UF, and 0.981 and 0.984 in RW, respectively. However, comparative statistical analysis using residual sum-of-squares (RSS) and ANOVA indicated that the PSO model provided a superior fit across both matrices ($p < 0.0001$). The PSO rate constants (k_2) in Medupi UF (Fig. 2b) followed the performance ranking: MPR1000 (0.072) > A860S (0.032) > A502PS (0.016 $\text{g mg}^{-1} \text{ min}^{-1}$). In Vaal RW, all resins exhibited strong PSO correlation

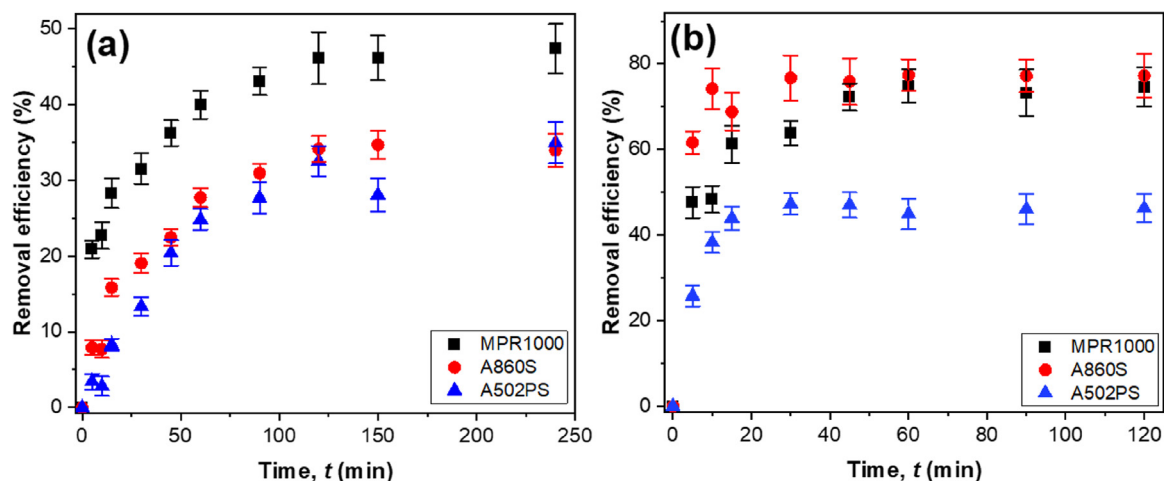


Fig. 1. Time-dependent dissolved organic carbon (DOC) removal efficiency using three strong base anion-exchange resins, MPR1000, A860S, and A502PS, for (a) Medupi ultrafiltrate (UF) and (b) Vaal River raw water (RW). The figure highlights the differences in removal kinetics and equilibrium efficiencies across resin types and water matrices, with faster and higher removal observed in Vaal RW due to lower competition from inorganic anions and higher NOM aromaticity.

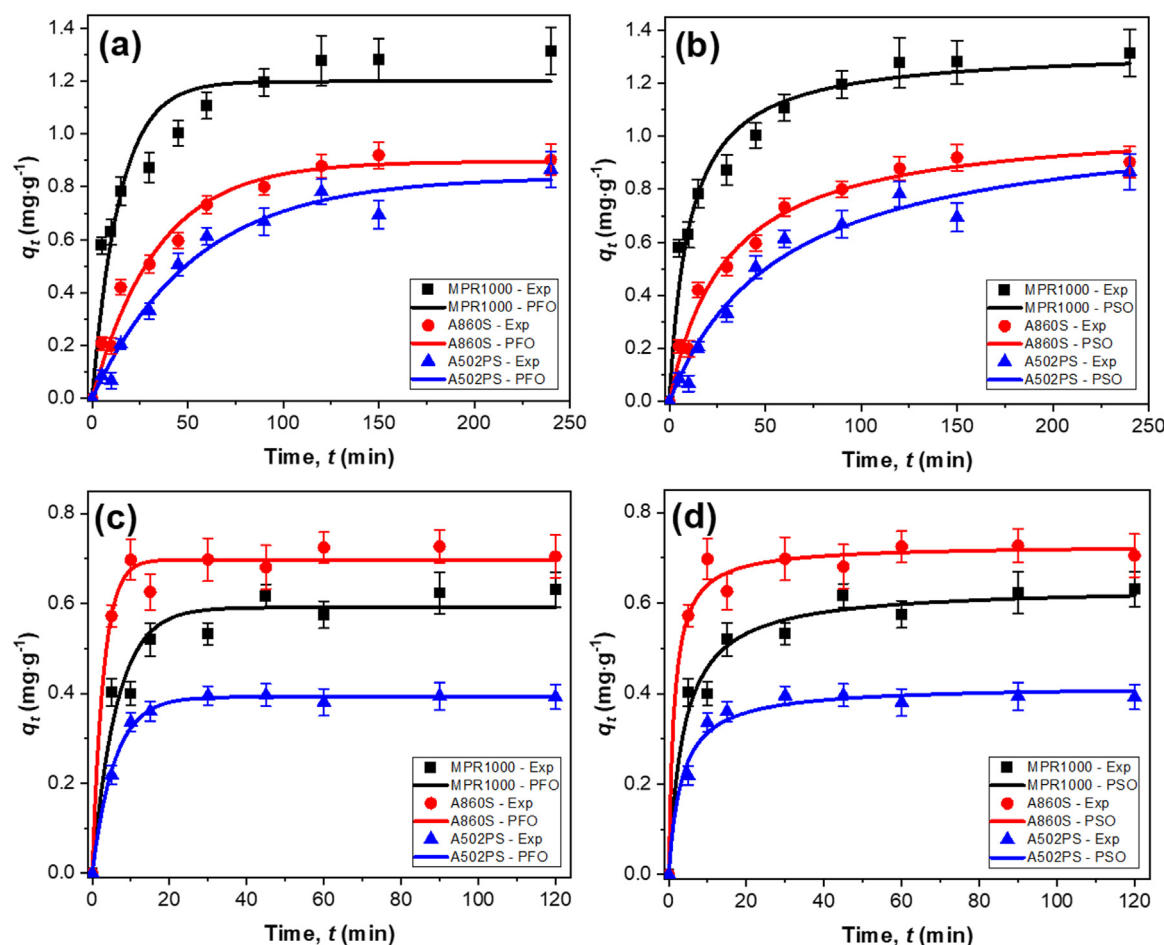


Fig. 2. Kinetic modelling of natural organic matter (NOM) adsorption from (a,b) Medupi ultrafiltrate (UF) and (c,d) Vaal raw water (RW) using macroporous anion exchange resins (MPR1000, A860S, A502PS). Experimental adsorption capacities (q_t) are compared with (a,c) pseudo-first-order (PFO) and (b,d) pseudo-second-order (PSO) model predictions. The PSO model generally demonstrates superior fit (Adj. $R^2 \geq 0.97$ across all systems), supporting chemisorption as the dominant dissolved organic carbon (DOC) removal mechanism. However, an exception for A502PS (UF and RW) is observed, where PFO is superior.

($R^2 > 0.97$) (Fig. 2d), with q_e values of 0.64 ± 0.02 (MPR1000), 0.73 ± 0.02 (A860S), and 0.42 ± 0.01 mg g⁻¹ (A502PS). The elevated rate constants observed in Vaal RW (0.41 – 1.0 g mg⁻¹ min⁻¹) compared to Medupi UF (0.02 – 0.07 g mg⁻¹ min⁻¹) are attributed to enhanced

mass transfer driving forces, resulting from higher resin dosage (5 vs. 2 g L⁻¹) and lower levels of competing anions. These findings demonstrate how the distinct resin physicochemical properties (Table 1), operational conditions, and water matrix characteristics (Table

Table 3
Nonlinear kinetic fits (PFO and PSO) for ion-exchange resins in Medupi ultrafiltrate (UF) and Vaal River raw water (RW).

Resin	Matrix	Model	q_e (mg g ⁻¹)	k	Adj. R^2	RSS	F	p
MPR1000	UF	PFO	1.22 ± 0.05	0.07 ± 0.01	0.908	0.15	422	2.19 × 10 ⁻¹⁰
		PSO	1.34 ± 0.04	0.07 ± 0.01	0.969	0.049	1277	9.03 × 10⁻¹³
	RW	PFO	0.59 ± 0.02	0.16 ± 0.03	0.936	0.018	462	3.70 × 10 ⁻⁸
		PSO	0.64 ± 0.02	0.41 ± 0.10	0.970	0.008	984	9.65 × 10⁻¹⁰
A860S	UF	PFO	0.90 ± 0.03	0.03 ± 0.00	0.973	0.025	804	7.16 × 10 ⁻¹¹
		PSO	1.06 ± 0.05	0.03 ± 0.01	0.980	0.019	1076	1.94 × 10⁻¹¹
	RW	PFO	0.70 ± 0.01	0.35 ± 0.05	0.981	0.007	1852	2.91 × 10 ⁻¹⁰
		PSO	0.73 ± 0.02	1.00 ± 0.27	0.984	0.006	2122	1.81 × 10⁻¹⁰
A520PS	UF	PFO	0.84 ± 0.04	0.02 ± 0.00	0.976	0.021	658	1.76 × 10⁻¹⁰
		PSO	1.08 ± 0.08	0.02 ± 0.00	0.971	0.025	545	4.07 × 10 ⁻¹⁰
	RW	PFO	0.39 ± 0.00	0.17 ± 0.01	0.996	0.0004	8449	1.44 × 10⁻¹²
		PSO	0.42 ± 0.01	0.72 ± 0.16	0.977	0.003	1315	9.65 × 10 ⁻¹⁰

Notes: Parameter values are given as estimate ± standard error from nonlinear regressions. PFO: k_1 in min⁻¹; PSO: k_2 in g mg⁻¹ min⁻¹. RSS = residual sum of squares; F and p from ANOVA. The PSO model generally provided the best fit across resins and matrices, except for A520PS (UF and RW), where PFO was superior; best-fitting model per resin × matrix is bolded.

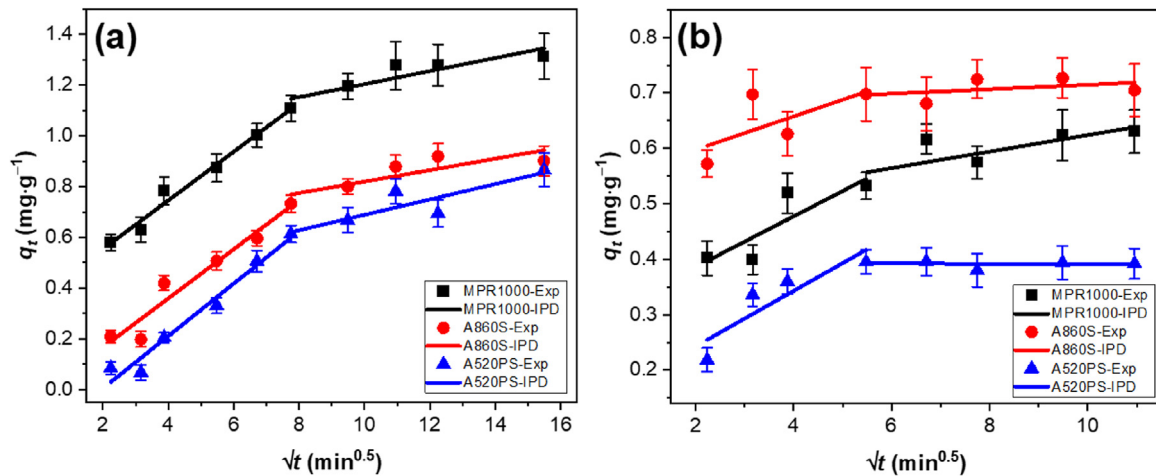


Fig. 3. Intraparticle diffusion (IPD) model of natural organic matter (NOM) adsorption in (a) Medupi ultrafiltrate (UF) and (b) Vaal raw water (RW) systems. The $q_t - \sqrt{t}$ dependence reveals film diffusion (Stage 1) and intraparticle diffusion (Stage 2).

Table 4
Intra-particle diffusion (IPD) analysis for ion-exchange resins in Medupi ultrafiltrate (UF) and Vaal River raw water (RW): two linear regimes fitted as $q_t = k_{id} t^{1/2} + C$. Where C is the boundary layer thickness (BLT).

Resin	Matrix	IPD stage	C (mg g ⁻¹)	k_{id} (mg g ⁻¹ min ^{-0.5})	Adj. R^2	RSS	F	p
MPR1000	UF	Stage 1	0.36 ± 0.03	0.096 ± 0.007	0.976	0.0041	207	1.35 × 10 ⁻⁴
		Stage 2	0.95 ± 0.08	0.026 ± 0.007	0.754	0.0051	13.2	3.58 × 10 ⁻²
	RW	Stage 1	0.29 ± 0.07	0.046 ± 0.019	0.613	0.0040	5.78	1.35 × 10 ⁻¹
		Stage 2	0.48 ± 0.06	0.015 ± 0.007	0.485	0.0026	4.76	1.17 × 10 ⁻¹
A860S	UF	Stage 1	-0.03 ± 0.06	0.097 ± 0.012	0.929	0.0130	66.8	1.22 × 10 ⁻³
		Stage 2	0.59 ± 0.09	0.023 ± 0.008	0.621	0.0070	7.55	7.09 × 10 ⁻²
	RW	Stage 1	0.54 ± 0.09	0.030 ± 0.023	0.186	0.0060	1.68	3.24 × 10 ⁻¹
		Stage 2	0.67 ± 0.04	0.004 ± 0.005	-0.061	0.0011	0.44	4.45 × 10 ⁻¹
A520PS	UF	Stage 1	-0.20 ± 0.05	0.103 ± 0.009	0.961	0.0078	124	2.69 × 10 ⁻⁴
		Stage 2	0.39 ± 0.10	0.030 ± 0.009	0.726	0.0082	11.6	4.23 × 10 ⁻²
	RW	Stage 1	0.14 ± 0.07	0.050 ± 0.018	0.699	0.0034	7.95	1.06 × 10 ⁻¹
		Stage 2	0.39 ± 0.01	-3.6 × 10 ⁻⁴ ± 0.002	-0.314	0.0016	0.45	8.46 × 10 ⁻¹

Notes: Stage 1 corresponds to the early, higher-slope regime (boundary-layer or film diffusion), while Stage 2 corresponds to the later regime (intra-particle diffusion). For several RW fits (A860S and A520PS), slopes were not significant at $\alpha = 0.05$, indicating that intra-particle diffusion was not the sole rate-limiting step. Slope significance was evaluated using ANOVA; non-significant p -values ($p > 0.05$) indicate that the IPD slope is not statistically different from zero.

2) collectively govern NOM removal efficiency and mechanism [35], emphasising the need for system-specific optimisation.

Although MPR1000 has the lowest ion-exchange capacity (0.65 eq L⁻¹), it achieved the highest adsorption capacity in Medupi UF ($q_e = 1.34$ mg g⁻¹), a performance driven by its hybrid polyacrylic/polystyrene matrix and intermediate water content (68%–74%) that synergistically optimised hydrophilicity and structural stability for

NOM uptake. The superior NOM removal performance of MPR1000 is inferred to arise from a synergistic effect that combines the distinct properties of its constituent resins, enhancing NOM diffusion and access to exchange sites. This is consistent with established principles of ion exchange, where the integration of different resin types provides broader contaminant coverage than single-resin systems [36, 37]. In particular, synergy at the polystyrene–polyacrylic interface

likely reflects the combined action of hydrophobic adsorption and hydrophilic ionic interactions, as highlighted in the literature [13,24]. However, this mechanistic interpretation remains inferential, as no surface or structural characterisation (e.g., BET surface area, pore size distribution, FTIR, XPS) was performed in the present study. Future investigations employing these and other complementary techniques (e.g., solid-state NMR, tracer studies) will be required to directly verify and further elucidate the physicochemical interactions between resin matrices and specific NOM fractions.

A860S demonstrated consistent performance across both water matrices ($q_e = 0.73\text{--}1.06\text{ mg g}^{-1}$), supported by its fully polyacrylic structure, water content (66%–72%), and optimal exchange capacity (0.80 eq L^{-1}). These features facilitated greater accessibility to charged NOM fractions and resilience to ionic interference, as reflected in its strong model fits ($R^2 > 0.98$). In contrast, A502PS exhibited the lowest adsorption capacity ($q_e = 0.42\text{--}1.08\text{ mg g}^{-1}$) despite having the highest exchange capacity (0.85 eq L^{-1}) and water content (70%–75%). Its rigid polystyrene matrix introduced steric limitations and restricted internal diffusion, particularly evident in Vaal RW, where a low intraparticle diffusion rate ($k_{id2} = -3.6 \times 10^{-4}\text{ mg g}^{-1}\text{ min}^{-0.5}$) and minimal boundary layer contributions (Fig. 3b) confirmed hindered mass transfer. The comparatively strong performance of MPR1000, despite its lower nominal capacity, underscores the critical role of matrix composition. Its dual polymer backbone likely enables interaction with both hydrophilic and hydrophobic NOM fractions, reducing electrostatic repulsion and enhancing overall uptake, a mechanism corroborated by Bolto et al. [23].

The enhanced removal observed in Vaal RW results from multiple compounding factors. First, A860S's hydrophilic polyacrylic matrix improves access to dissolved organics in aqueous media [38]. Second, the higher initial DOC concentration and resin dosage increased the mass transfer driving force, thereby accelerating adsorption kinetics. Third, the significantly lower sulphate content in Vaal RW (13 vs. 172 mg L^{-1} in Medupi UF) reduced competition for active sites, improving NOM binding efficiency [39,40]. Lastly, differences in NOM composition played a pivotal role - Vaal RW exhibited greater aromaticity ($\text{SUVA}_{254} = 3.1\text{ L mg}^{-1}\text{ m}^{-1}$) compared to Medupi UF ($2.0\text{ L mg}^{-1}\text{ m}^{-1}$), favouring adsorption due to enhanced interaction with delocalised π -electrons in aromatic structures [41]. Conversely, Medupi UF's higher ionic strength ($5.45\text{ vs. }1.55\text{ meq L}^{-1}$) and the predominance of more hydrophilic, low-aromatic NOM fractions likely suppressed resin–NOM interactions.

The IPD model revealed biphasic kinetics for all systems (Fig. 3) [34,42], with all resins exhibiting superior performance in Medupi UF ($k_{id1} = 0.096\text{--}0.103\text{ mg g}^{-1}\text{ min}^{-0.5}$) (Fig. 3a), highlighting their suitability for low-aromatic NOM removal. In contrast, A502PS's extremely low IPD rates underscored its matrix limitations. The two-stage IPD plots indicated sequential mass transfer mechanisms: initial rapid film diffusion followed by slower intraparticle diffusion, consistent with observations by Fierro et al. [43]. The distinct linear segments in both water matrices confirmed the multi-stage nature of the adsorption process, with initial macroporous diffusion preceding slower micropore penetration. Critically, none of the regression lines intersected the origin, confirming the influence of external mass transfer. The boundary layer thickness (BLT), inferred from the y-intercepts, was highest for MPR1000 (0.36 ± 0.03) in Medupi UF and A860S (0.54 ± 0.09) in Vaal RW, suggesting greater resistance to film diffusion [44].

The IPD model produced a negative BLT for A860S and A502PS in Medupi UF, a phenomenon also reported in other studies (e.g., Lu et al. [45]). The interpretation of BLT values, particularly negative estimates, warrants careful consideration. As Wang and Guo [46] emphasise, negative BLT values are not physically meaningful but may arise from propagated error during linearisation, especially at early time points where measurement uncertainty in $\sqrt{t}$ is magnified (Fig. 3). In the present study, such values are observed in Stage 1 fits of the IPD model and are best understood as artifacts of model-fitting rather than indicators of a physically negative boundary layer. Mechanistically,

negative or near-zero BLT values may suggest negligible film diffusion resistance, with adsorption dominated by intraparticle or surface diffusion processes. This interpretation is supported by the moderate adjusted R^2 values and the absence of origin-passing regression lines in Stage 1, indicating that external mass transfer is not rate-limiting under the tested conditions.

Stage-2 IPD fits, which represent the later adsorption regime, yielded consistently low boundary layer constants ($\text{BLT} < 1\text{ mg g}^{-1}$) across both water matrices. For Vaal RW, all three resins produced weak or nonphysical slopes with poor statistical support: A520PS gave a negative slope ($k_{id2} = -3.6 \times 10^{-4}\text{ mg g}^{-1}\text{ min}^{-0.5}$, adj. $R^2 = -0.314$, $p = 0.85$), while A860S and MPR1000 had small positive slopes (0.004 and $0.015\text{ mg g}^{-1}\text{ min}^{-0.5}$, respectively) but non-significant fits ($p = 0.45$ and 0.12). These results indicate that intraparticle diffusion was not the rate-limiting step in RW. In Medupi UF, the Stage-2 regressions were somewhat stronger: MPR1000 ($k_{id2} = 0.026$, adj. $R^2 = 0.754$, $p = 0.036$) and A520PS ($k_{id2} = 0.030$, adj. $R^2 = 0.726$, $p = 0.042$) yielded statistically significant fits, suggesting a modest contribution of intraparticle diffusion to the late adsorption stage. By contrast, A860S produced a weaker, non-significant slope ($k_{id2} = 0.023$, adj. $R^2 = 0.621$, $p = 0.071$).

ANOVA results (Table 4) showed non-significant p -values in several raw water fits (e.g., A860S and A520PS), indicating that intraparticle diffusion alone did not govern the adsorption kinetics. More broadly, ANOVA results (Tables 3 and 4) confirmed that observed differences in resin performance and kinetic model fits were statistically significant in most cases ($p < 0.05$), thereby supporting the comparative conclusions drawn from DOC removal and model fitting analyses. Overall, the IPD model suggests that diffusion contributes only a minor or supportive role in the later stages of NOM uptake, more apparent in Medupi UF than in Vaal RW, but never as the sole rate-controlling mechanism. To provide a broader mechanistic perspective, nonlinear kinetic models (PFO and PSO) were also applied (Table 3). The PSO model generally offered superior fits across resin–matrix combinations, except A520PS in RW, where PFO was favoured. These results reinforce the multi-step nature of the adsorption process and highlight the importance of using multiple models and statistical criteria – such as adjusted R^2 , RSS, and ANOVA – to comprehensively evaluate kinetic behaviour.

Taken together, these findings demonstrate that the IPD model alone cannot fully characterise mass transfer, and that concurrent processes captured by PFO and PSO models also contribute to NOM uptake. BLT values should therefore be interpreted in the context of model fit quality and mechanistic plausibility rather than as standalone indicators of boundary layer behaviour. Future studies may benefit from time-resolved modelling and complementary approaches (e.g., tracer studies or microfluidic visualisation) to further elucidate mass transfer dynamics in ion-exchange systems.

The observed variability in rate constants among the resins suggests differences in macro- and micropore distribution and total pore volume, significantly impacting NOM uptake. Since all resins shared the same particle size range ($425\text{--}1200\text{ }\mu\text{m}$), this factor was ruled out as a contributor to the differing adsorption rates. Instead, resin capacity, water content, backbone composition, and pore structure must be considered to explain performance variations fully. Resin dosage had a notable impact on adsorption performance, with 2 g L^{-1} used for Medupi UF and 5 g L^{-1} for Vaal RW to account for differences in their TOC concentrations ($4.3\text{ vs. }5.2\text{ mg L}^{-1}$) and turbidity levels ($1.5\text{ vs. }84.1\text{ NTU}$). Adsorption performance was normalised to milligrams of DOC removed per gram of resin (i.e., specific adsorption capacity; see Table 3) to facilitate meaningful cross-matrix comparisons. This normalisation minimises the confounding influence of dosage variation, allowing performance trends to reflect intrinsic resin behaviour rather than mass loading effects. Notably, the dosage variation also yielded secondary mechanistic insights. In Vaal River water, the higher resin loading increased the number of available exchange sites but did not proportionally enhance per-gram adsorption capacity, suggesting

partial site saturation and a diminished mass transfer driving force. Conversely, the lower dosage applied to Medupi UF promoted more efficient site utilisation and accelerated uptake, highlighting trade-offs between resin loading, adsorption efficiency, and kinetic response.

In keeping with the study's emphasis on operational realism, all adsorption experiments were conducted at the intrinsic pH of the source waters rather than under optimised conditions. While this approach reduces pretreatment requirements and better reflects practical implementation scenarios, it is acknowledged that the absence of pH control limits mechanistic resolution. Future investigations should incorporate systematic pH adjustment to more directly evaluate the role of protonation dynamics and functional group interactions in NOM–resin binding.

LC-OCD analysis revealed that NOM in Medupi UF and Vaal RW exhibited similar molecular weight distributions, with humic substances comprising the most significant fraction (~60% of CDOC), followed by building blocks and low molecular weight (LMW) neutrals (Fig. 4). Although absolute concentrations varied, the relative distributions were largely consistent: biopolymers accounted for 4.18% in Medupi UF and 3.12% in Vaal RW. Trace amounts of biopolymers were detected in the Medupi UF permeate, despite the expectation that UF membranes should retain most macromolecular fractions. This partial breakthrough aligns with findings by Hidayah et al. [47], who reported UF removal efficiencies of approximately 94%–96% for biopolymer fractions, resulting in a residual 4%–6% presence in the permeate. It should be noted that the UF performance was not optimised or validated under controlled laboratory conditions, as the permeate was collected directly from the power plant and analysed as received. While building blocks were slightly more abundant in Medupi UF (22.95% vs. 20.07%). The greater proportion of smaller, more hydrophilic building blocks in Medupi UF, coupled with its lower SUVA₂₅₄ value (2.03 vs. 3.08 L mg⁻¹ m⁻¹), suggests improved NOM accessibility for adsorption, particularly with macroporous resins. Nonetheless, these compositional differences alone do not fully account for the variations in DOC removal efficiency across the resins, highlighting the additional influence of water matrix characteristics and resin physicochemical properties. Supporting Information Table S1 summarises the NOM fraction distributions for Medupi UF and Vaal RW as determined by LC-OCD, including CDOC concentrations, SUVA₂₅₄ values, and the relative contributions of biopolymers, humic substances, building blocks, and LMW fractions.

In the untreated Vaal River sample, the LC-OCD signal did not yield quantifiable hydrophobic organic carbon (HOC). It should be noted that LC-OCD operationally defines HOC as the difference between DOC and CDOC, representing material not eluted from the column. Therefore, this does not directly reflect the hydrophobicity of NOM. Literature reports suggest that river waters typically contain 1%–10% HOC by LC-OCD [31], while resin fractionation studies indicate that more than 50% of river water NOM can be hydrophobic in nature [17]. For this reason, we interpret HOC values cautiously and do not rely on them as a primary indicator of hydrophobic NOM removal.

Time-resolved LC-OCD analysis of Medupi UF treated with the polyacrylic resin A860S revealed distinct removal patterns for five NOM fractions over a 240 min contact period (Fig. 5), illustrating both the resin's selectivity and kinetic limitations. Biopolymers (P1), comprising approximately 4% of the chromatographable dissolved organic carbon (CDOC), showed minimal removal due to their large molecular size and limited access to the resin's internal pore network. Although their low initial concentration (0.12 mg L⁻¹) had little impact on overall DOC removal, elevated levels could contribute to pore blockage over time, a critical factor for long-term resin operation. In contrast, humic substances (P2), which accounted for the majority of CDOC (~62%), were rapidly and efficiently removed, achieving over 80% reduction within the first 60 min [48]. This high removal efficiency reflects strong electrostatic interactions between the resin's quaternary ammonium groups and the aromatic, acidic functionalities of humic compounds.

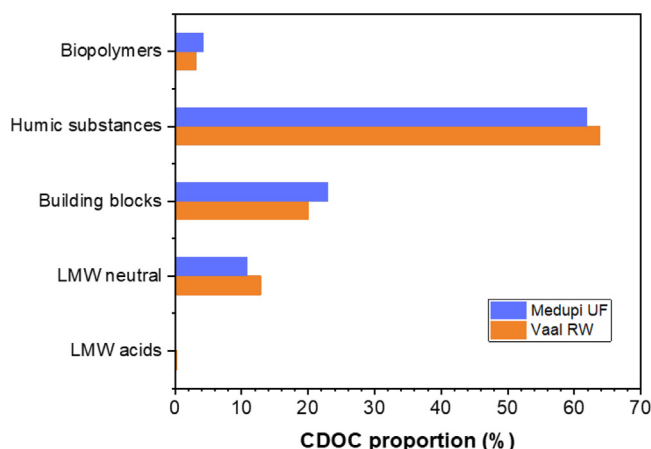


Fig. 4. LC-OCD analysis of chromatographable dissolved organic carbon (CDOC) fractions in Medupi UF and Vaal RW, showing the relative abundance of biopolymers, humic substances, building blocks, LMW acids (< 0.3%), and LMW neutrals. While both source waters display comparable NOM profiles, Medupi UF contains elevated building blocks with lower humics and LMW neutrals compared to Vaal RW, reflecting differences in aromaticity (SUVA₂₅₄: 2.03 vs. 3.08 L mg⁻¹ m⁻¹).

The rapid equilibration observed suggests that shorter contact times may suffice for humic-rich waters, potentially enabling more compact and cost-effective system designs.

Building blocks (P3), representing about 23% of CDOC, were removed to a moderate extent (~54%), likely constrained by steric effects and lower charge density compared to humics. This partial uptake underscores the role of molecular structure and ionisability in determining ion-exchange performance. Conversely, low molecular weight (LMW) acids and humics (P4) [31] showed limited removal (< 20%), consistent with their low anionic character and high hydrophilicity, which reduce their affinity for the resin's active sites. LMW neutrals (P5), being uncharged, exhibited negligible removal as expected.

The results confirm that A860S is particularly effective for selectively targeting charged, high-molecular-weight NOM fractions such as humic substances but is considerably less effective for low-charge or neutral components. This selective removal profile suggests that while ion exchange can serve as an efficient treatment option for humic-dominated waters, achieving comprehensive NOM removal may require complementary processes such as activated carbon adsorption or ozonation [38]. Moreover, the observed fraction-specific removal kinetics emphasise the importance of tailoring operational parameters – such as resin dosage and contact time – to the dominant NOM fractions present in the source water, which is essential for optimising treatment performance and ensuring compliance with water quality standards.

It should be noted that LC-OCD fractionation was conducted only for the A860S–Medupi UF system, selected for its removal profile and relevance to mechanistic interpretation. While this limits direct comparison across all resins, the targeted analysis nonetheless provides valuable fraction-specific insights that complement bulk DOC data. Future studies will extend LC-OCD to other resin–water systems, enabling a more comprehensive mechanistic evaluation.

Overall, the results highlight that resin performance is governed by a nuanced interplay between polymer matrix characteristics, such as structural flexibility and hydration capacity, and source water chemistry, including NOM composition and ionic strength. Among the tested resins, A860S emerged as the most versatile, likely due to its balanced hydrophilic–hydrophobic profile and favourable water content, which facilitated consistent performance across both water types. In contrast, MPR1000 and A502PS exhibited matrix-specific suitability, with MPR1000 performing optimally in low-ionic-strength, hydrophilic

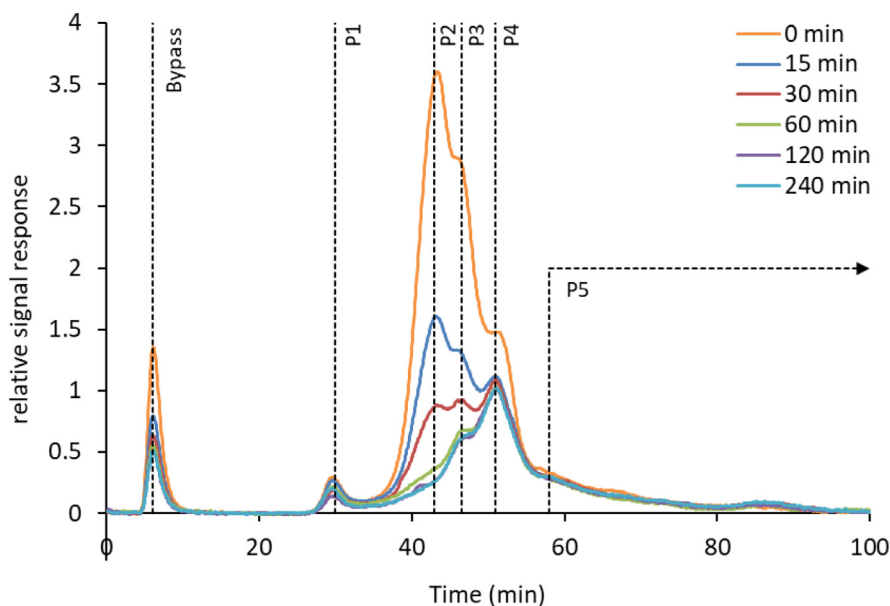


Fig. 5. Time-resolved LC-OCD chromatograms of Medupi UF during treatment with A860S resin, showing differential removal kinetics across NOM fractions: (P1) biopolymers, (P2) humic substances, (P3) building blocks, (P4) LMW acids, and (P5) LMW neutrals. The rapid depletion of P2 and P3 contrasts with the persistence of P1 and P5, demonstrating a fraction-dependent affinity for quaternary ammonium sites. The time sequence reveals distinct kinetic phases corresponding to film diffusion (0–60 min) and intraparticle diffusion (> 60 min) regimes.

NOM environments and A502PS showing limited efficacy due to diffusional constraints imposed by its rigid polystyrene structure.

The consistent dominance of the PSO model across all systems confirms chemisorption as the primary mechanism of NOM removal. However, the relative influence of physical adsorption appears to vary, particularly in the case of A502PS, where the closer alignment with PFO kinetics suggests a greater role for surface adsorption processes. These distinctions carry important practical implications: effective resin selection must consider both the composition of the target water, such as SUVA₂₅₄ values and concentrations of competing anions, and the specific treatment objectives, whether prioritising rapid adsorption kinetics or maximising equilibrium capacity.

The observed kinetic profiles also suggest that intraparticle diffusion contributes significantly to rate limitation, but it does not act in isolation. Additional mass transfer mechanisms, including boundary layer resistance at the resin–solution interface and competitive adsorption dynamics, are likely at play and warrant further investigation. A deeper understanding of these interfacial phenomena is essential for optimising ion exchange system performance, particularly under variable conditions typical of thermal power generation water cycles. Future research will focus on unravelling these complex interactions to support the development of predictive models and the design of more effective, hybrid treatment solutions tailored to diverse water quality scenarios.

3.4. Regeneration and long-term performance

The long-term operation of ion-exchange resins depends strongly on effective regeneration and fouling control. Although this study did not include multi-cycle testing, manufacturer datasheets and peer-reviewed studies provide practical insights into expected performance. The A860S resin is regenerated with ~10% NaCl brine, supplemented with a small addition of NaOH when organic fouling accumulates. The Purolite datasheet specifies up-flow backwash with 50%–70% bed expansion for 10–15 min (~30 min at startup) to control pressure drop and reclassify the bed. Independent testing has confirmed its regeneration efficiency. Bazri et al. [49] compared A860 with a weak-base resin under consecutive batch loadings. They reported a ~95% regeneration efficiency with NaCl brine, which is ~20% higher than that of the weak-base counterpart. These findings underscore that A860 not only

regenerates effectively but also sustains NOM removal capacity over multiple cycles. Recent mechanistic studies further confirm that resin functional groups and backbone chemistry govern long-term removal patterns, with polyacrylic resins generally more resistant to organic fouling than polystyrenic ones [50].

Literature consistently reports A520PS regeneration with NaCl brine in the 0.6–1.0 M range. For example, Zareie et al. [51] regenerated the resin with 1 M NaCl for 60 min and demonstrated effective reuse over seven cycles, with no significant decline in nitrate removal efficiency. Acid/base conditioning (1 M NaOH, 0.1 M HCl) has also been reported to restore performance in cases of fouling. Reported nitrate capacities (18–33 mg N g⁻¹ in batch and column studies) align with the manufacturer's total exchange capacity (~39 mg N g⁻¹ dry basis), suggesting that appropriate regeneration maintains functional capacity over time [51–53]. Beyond nitrate systems, long-term column studies emphasise that electrostatic exchange dominates after multiple regeneration cycles, while non-electrostatic interactions gradually diminish [50], reinforcing the need for effective fouling control.

The MPR1000 hybrid resin blend is designed for pretreatment of feedwater with elevated organic and colloidal loads. Regeneration protocols for such resins typically involve high-concentration brine combined with caustic agents to address both ionic displacement and organic fouling. While specific multi-cycle performance data for MPR1000 are limited in the public domain, manufacturer guidance suggests that aggressive regeneration – often incorporating sodium hydroxide – helps mitigate capacity loss associated with organic contamination. Recent advances highlight that regeneration strategies themselves strongly influence long-term viability. For instance, segmented regeneration has been shown to recover NOM and sulphate more selectively, thereby improving salt efficiency by ~21% compared to conventional regeneration [54]. Such strategies not only sustain resin performance but also alleviate brine management challenges, which remain a critical barrier for large-scale ion exchange applications [55].

Across all three resins, consistent backwashing, proper regenerant dosing, and monitoring of leakage and pressure drop are central to maintaining long-term performance. Literature reports suggest that strong-base resins can retain over 90% of their functional capacity after multiple regeneration cycles when operated under optimal conditions [49,50]. Organic fouling remains the main factor in capacity

decline, highlighting the need for fouling control and optimised regeneration strategies. While empirical multi-cycle validation remains a priority for future work, current evidence indicates that the resins evaluated are industrially viable for NOM-rich power plant waters.

3.5. Economic considerations and industrial implications

From an economic perspective, approximate resin costs and operational parameters have been compiled in the Supporting Information (Tables S2 and S2a). Local pricing for A502PS and A860S was approximately R 67/L (~US\$ 3.4/L) and R 125/L (~US\$ 6.4/L), respectively. Regeneration for both resins typically requires 10% NaCl brine, optionally supplemented with NaOH. Resin lifetime is highly dependent on operational usage and source water quality. Reported estimates therefore vary, ranging from 18–24 months in demanding applications such as sugar processing to 4–5 years in demineralisation systems with less complex feedwaters.

While A860S is more expensive, its superior selectivity for charged NOM fractions makes it attractive for applications requiring stringent NOM control. In contrast, the lower cost of A502PS renders it a viable and cost-effective option for treating waters with lower aromaticity. Although MPR1000 has been discontinued internationally and is no longer commercially available, it provides valuable insight into the synergistic behaviour of mixed polystyrenic–polyacrylic resins. These findings highlight the importance of balancing initial performance with long-term lifecycle costs and regeneration demands when evaluating industrial-scale implementation, particularly in power plant water treatment where consistent water quality is critical.

4. Conclusion

This study demonstrates that the performance of ion-exchange resins in removing NOM is critically governed by the interplay between material properties and water matrix characteristics, with direct implications for thermal power generation. The MPR1000's hybrid polyacrylic/polystyrene matrix achieved superior DOC uptake ($q_e = 1.34 \text{ mg g}^{-1}$) in low-ionic-strength waters, such as ultrafiltered boiler feedwater (Medupi UF), highlighting its suitability for pretreatment in high-purity steam cycles. However, the polyacrylic-based A860S emerged as the most industrially viable option, delivering consistent performance ($q_e = 0.73\text{--}1.06 \text{ mg g}^{-1}$) across diverse water chemistries – including sulphate-rich cooling tower blowdown (Vaal RW) – due to its hydrated network (66%–72% water content) and resilience to ionic competition. This versatility is critical for power plants managing variable water sources, where fluctuating organic and inorganic loads demand robust treatment solutions. In contrast, the polystyrene-based A502PS, despite its high exchange capacity, suffered from severe diffusional limitations ($k_{id1} = 0.004 \text{ mg g}^{-1} \text{ min}^{-0.5}$), underscoring the operational risks of prioritising chemical stability over kinetic performance in high-fouling environments.

Kinetic and LC-OCD analyses revealed the preferential removal of humic substances, but limited reduction of biopolymers, a finding with significant implications for power plant cycle chemistry. The persistence of high-MW organics poses a risk to membrane fouling and steam purity compromises, suggesting that ion exchange should be paired with complementary techniques (e.g., activated carbon adsorption, coagulation or advanced oxidation) for comprehensive NOM control. Moreover, the dominance of chemisorption ($\text{PSO } R^2 \geq 0.97$) and multiphase diffusion pathways necessitates careful resin regeneration protocols to maintain capacity amid cyclic thermal stresses.

These insights emphasise that effective NOM removal via ion exchange requires careful alignment between resin physicochemical properties and target water characteristics. For thermal power applications, where high sulphate levels and diverse NOM fractions are common, resin selection and system design must consider kinetic limitations, diffusion pathways, and NOM speciation. Future work should focus

on tailored resin architectures that combine high selectivity for NOM with resilience to inorganic competition, exploring resin regeneration efficiency and hybrid treatment configurations to enhance the applicability of ion exchange in complex water treatment scenarios for thermal power generation.

CRedit authorship contribution statement

Tebogo Tseka: Writing – original draft, Visualization, Methodology, Data curation, Conceptualization. **Pascal Finkbeiner:** Writing – original draft, Writing – review & editing, Validation, Formal analysis. **Zebron Phiri:** Writing – review & editing, Visualization, Validation, Software, Formal analysis, Data curation. **Thabo T.I. Nkambule:** Writing – review & editing, Supervision, Resources, Funding acquisition. **Peter Jarvis:** Writing – review & editing, Supervision, Resources, Project administration. **Lueta-Ann de Kock:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.jwpe.2025.108829>.

Data availability

Data will be made available on request.

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