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Removal of antibiotic contaminants from water via adsorption: Analysis of equilibrium isotherms

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ABSTRACT

In this study, we evaluated the performance of three related isotherm models—the Dubinin–Radushkevich (DR), Dubinin–Radushkevich–Misra (DRM), and Dubinin–Astakhov (DA) equations—for describing the adsorption of antibiotic contaminants from water, including tetracycline, metronidazole, ofloxacin, ciprofloxacin, and chlortetracycline. We applied the models to published datasets exhibiting favorable (type I) and sigmoidal (type V) isotherm profiles. The DA and DRM equations are shown to consistently outperform the DR equation, providing maximum adsorption capacity estimates that more closely match experimental values, whereas the DR equation is shown to yield unrealistic predictions. These findings suggest that the DA and DRM equations offer more reliable alternatives to the commonly used DR equation for modeling antibiotic adsorption equilibria. Of the two, the DRM equation has practical appeal because it does not require solubility data. However, when applied to type V isotherms, some of its parameters cannot be reliably estimated, limiting its applicability.

1. Introduction

Measuring and interpreting adsorption equilibrium data is a core component of adsorption research. In water contaminant adsorption studies, equilibrium behavior is typically described using explicit algebraic expressions, most commonly through simple two-parameter isotherm models such as the Freundlich and Langmuir equations. In addition to these well-established models, other two-parameter isotherms are increasingly employed to fit experimental data, with the Dubinin–Radushkevich (DR) equation being a prominent example. The DR model has been widely applied in studies of organic micropollutant adsorption, including antibiotics, onto a variety of adsorbents, offering a straightforward method for data fitting. Table 1 summarizes selected studies that have used the DR equation to model antibiotic adsorption [1–13]. Like the Freundlich and Langmuir equations, the DR model can be linearized, allowing for convenient parameter estimation via linear regression.

The Dubinin–Astakhov (DA) isotherm is a generalized extension of the DR equation, incorporating an additional adjustable parameter to provide greater flexibility in fitting adsorption data. Despite its improved modeling capability, the DA equation has seen relatively limited use in antibiotic adsorption studies, with selected examples listed in Table 1 [14–26]. This limited adoption is largely attributed to its reliance on nonlinear regression for parameter estimation, a step that some researchers avoid, even though modern scientific software supports such analysis.

In addition to the DR and DA equations, this study considers the Dubinin–Radushkevich–Misra (DRM) isotherm, a rarely used variant of the DR model. Originally developed to describe gas adsorption on heterogeneous surfaces, the DRM equation introduces an additional adjustable parameter, enhancing model flexibility in a manner similar to the DA equation. It was first proposed as a global isotherm for deriving site energy distribution functions via the Stieltjes transform method. Like the DA equation, the DRM equation requires nonlinear regression for parameter estimation.

The DR, DA, and DRM models have not been systematically compared using adsorption data that span distinct isotherm types. In particular, their performance against sigmoidal (type V) isotherms remains largely unexamined, limiting our understanding of their applicability to systems that exhibit such adsorption behavior. This study addresses this gap by providing a comparative evaluation of the three isotherm models using published adsorption data for five antibiotic contaminants: tetracycline hydrochloride [3], metronidazole [4], ofloxacin

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Table 1
Selected examples of antibiotic adsorption data modeled using the DR and DA equations.

DR			DA		
Antibiotic	Adsorbent	Ref.	Antibiotic	Adsorbent	Ref.
Ofloxacin	Clay	Antonelli et al. [1]	Sulfamethoxazole	Biochar	Zheng et al. [14]
Tetracycline; ciprofloxacin	Strontium aluminate	Turan et al. [2]	Ciprofloxacin	Carbon nanotube	Li et al. [15]
Tetracycline	Porous carbon	Zhang et al. [3]	Norfloxacin	Porous carbon	Chen et al. [16]
Amoxicillin; metronidazole	Activated carbon	El Farissi et al. [4]	Norfloxacin	Barley straw	Yan and Niu [17]
Amoxicillin; ciprofloxacin; tetracycline	Biocomposite	Mirizadeh et al. [5]	Sulfamethoxazole	Activated carbon	Bizi [18]
Amoxicillin	Activated carbon	Dolfini et al. [6]	Ciprofloxacin	Clay mineral	Bizi and El Bachra [19]
Ampicillin	Lignocellulosic fiber	da Costa et al. [7]	Oxytetracycline	Photocatalyst	Xu et al. [20]
Ciprofloxacin	Polymer composite	Yılmazoğlu and Demircivi [8]	Ciprofloxacin; sulfadiazine; sulfamethoxazole; tetracycline	Biochar	Zhang et al. [21]
Cefuroxime	Dolomite	Türk Baydır et al. [9]	Cephalexin	Activated carbon	Wernke et al. [22]
Norfloxacin	Biochar	Zhou et al. [10]	Tetracycline	Biochar	Zaib et al. [23]
Tetracycline	Hydroxyapatite	Kanmaz and Demircivi [11]	Sulfamethoxazole	Biochar	Qiu et al. [24]
Tetracycline	Diatomite	Nguyen et al. [12]	Sulfamethazine; sulfamethoxazole; tinidazole	Microplastic	Zhang et al. [25]
Ofloxacin; enrofloxacin; lomefloxacin; difluorofloxacin	Polymer	Kang et al. [13]	Sulfamethoxazole; ciprofloxacin	Pyrolytic carbon	Ling et al. [26]

[1], ciprofloxacin hydrochloride [27], and chlortetracycline hydrochloride [28]. The first three exhibit favorable (type I) isotherms, while the latter two display sigmoidal (type V) behavior. The inclusion of type V isotherms offers a novel and rigorous benchmark for assessing the strengths and limitations of the three models across a broader range of adsorption phenomena.

2. Isotherm models and model fitting

2.1. Dubinin–Radushkevich (DR) equation

The commonly used form of the DR equation for liquid phase adsorption is shown in Eq. (1). In this expression, q represents the equilibrium amount adsorbed, q_m is the maximum adsorption capacity, c is the equilibrium concentration in the liquid phase, c_s is the solute solubility, and b is a dimensionless constant defined as $b = RT/E_a$, where R is the universal gas constant, T is the absolute temperature, and E_a is the characteristic adsorption energy. Contrary to common interpretations, E_a cannot reliably distinguish between physisorption and chemisorption mechanisms [29] and is best regarded as an empirical fitting parameter. Eq. (1) is valid up to the saturation point ($c \leq c_s$).

$$q = q_m \exp\left\{-\left[b\ln\left(\frac{c_s}{c}\right)\right]^2\right\} \tag{1}$$

The DR equation, derived from the Dubinin–Polanyi theory of micropore filling, is widely used to describe the adsorption of vapors and gases on microporous materials such as activated carbon [30]. Over time, various extensions and modifications have been proposed to overcome its limitations [31,32]. In adsorption studies, Eq. (1) is often rearranged into the linearized form shown in Eq. (2). This transformation implies that plotting $\ln(q)$ against $(\ln(c_s/c))^2$ yields a straight line with slope $-b^2$ and intercept $\ln(q_m)$. This linear relationship is commonly referred to as the characteristic curve.

$$\ln(q) = \ln(q_m) - \left[b\ln\left(\frac{c_s}{c}\right)\right]^2 \tag{2}$$

2.2. Dubinin–Astakhov (DA) equation

The DA equation is an extension of the DR equation [30], derived by replacing the fixed exponent "2" in the DR model with n, an adjustable parameter, as shown in Eq. (3). The parameter n accounts for the energetic heterogeneity of the adsorbent surface. Similar to the DR equation, the DA equation is often log-transformed to generate its characteristic curve, as expressed in Eq. (4).

$$q = q_m \exp\left\{-\left[b\ln\left(\frac{c_s}{c}\right)\right]^n\right\} \tag{3}$$

$$\ln(q) = \ln(q_m) - \left[b\ln\left(\frac{c_s}{c}\right)\right]^n \tag{4}$$

With three adjustable parameters (q_m, b, and n), the DA equation offers greater flexibility than the DR model, enabling it to accommodate a broader range of experimental isotherms. When $n = 1$, the DA equation reduces to the Freundlich isotherm. In recent studies, the DA equation is typically fitted to experimental data using nonlinear regression. For example, it has been applied to various equilibrium isotherms in ion-exchange systems to estimate representative values of n [33].

The DA equation is mathematically equivalent to the Polanyi–Dubinin, Polanyi–Manes, and Polanyi–Dubinin–Manes models, which are commonly used in environmental adsorption studies [34–37]. While the DR and DA equations are primarily empirical and useful for data correlation, they also share a common connection with an isotherm model derived from statistical mechanical principles [38].

2.3. Dubinin–Radushkevich–Misra (DRM) equation

The DRM equation, introduced by Misra in 1969 [39], was originally formulated to describe vapor adsorption on heterogeneous surfaces and was later adapted for liquid phase adsorption [40,41]. As shown in Eq. (5), it extends the DR equation by incorporating an additional fitting parameter, a, thereby increasing its flexibility. Like the DA model, the DRM equation includes three adjustable parameters (q_m, a, and b) and requires nonlinear regression for parameter estimation. A key distinction is that, unlike the DR and DA equations, the DRM model does not rely on solute solubility (c_s), which simplifies its application to experimental data. Despite being proposed more than five decades ago, the DRM equation remains largely overlooked in adsorption research [40,41].

$$q = q_m \exp\left\{-\left[b\ln\left(1 + \frac{a}{c}\right)\right]^2\right\} \tag{5}$$

2.4. Model fitting and performance evaluation

The three isotherm models were fitted to previously published equilibrium data for antibiotic adsorption using nonlinear regression implemented in GraphPad Prism. To ensure robust and reproducible parameter estimation, multiple sets of initial guesses were tested within plausible bounds for each model parameter. The selection of starting values was guided by parameter ranges reported in the literature and by visual inspection of the experimental data trends. Model performance was assessed using the root mean square error (RMSE), as defined in Eq. (6). In this equation, E_i is the experimentally measured q at data point i, M_i is the corresponding model-predicted q, z is the total number of data points, and p is the number of adjustable parameters.

$$\mathrm{RMSE} = \sqrt{\frac{\sum_{i=1}^{z}(E_i - M_i)^2}{z - p}} \tag{6}$$

In addition to the RMSE, the Akaike weight (AW) was used to compare model performance by accounting for both goodness of fit and model complexity. The AW indicator, defined by Eqs. (7) and (8), incorporates the corrected Akaike Information Criterion (AIC), the AIC value for the j-th model (AIC_j), the minimum AIC among all models (AIC_{min}), the AIC value for the k-th model (AIC_k), and the total number of competing models (w). The AW provides an estimate of the probability that the model with the lowest AIC value is the most appropriate choice.

$$\mathrm{AIC} = z\ln\left[\frac{1}{z}\sum_{i=1}^{z}(E_i - M_i)^2\right] + \frac{2z(p+1)}{z-p-2} \tag{7}$$

$$\mathrm{AW} = 100\frac{\exp[-0.5(\mathrm{AIC}_j - \mathrm{AIC}_{min})]}{\sum_{k=1}^{w}\exp[-0.5(\mathrm{AIC}_k - \mathrm{AIC}_{min})]} \tag{8}$$

3. Results and discussion

This study presents a comprehensive evaluation of the DR, DA, and DRM equations for modeling type I and type V isotherms in the adsorption of antibiotics on various adsorbents. The analysis draws on published datasets for the adsorption of tetracycline hydrochloride [3], metronidazole [4], ofloxacin [1], ciprofloxacin hydrochloride [27], and chlortetracycline hydrochloride [28] from aqueous solutions.

3.1. Type I isotherms

3.1.1. Case 1: adsorption of tetracycline hydrochloride on porous carbon

This case examines the adsorption of tetracycline hydrochloride from aqueous solutions, based on the study by Zhang et al. [3] (see the Supplementary Material for details). Tetracycline is widely used in human and veterinary medicine to treat bacterial infections; however, its extensive use and improper disposal have contributed to its persistent presence in aquatic environments.

Table 2
Model parameters and fit statistics for tetracycline hydrochloride adsorption on porous carbon [3].[a]

Parameter/fit metric	Isotherm model		
	DR	DA	DRM
q_m (mg g^{-1})	108.1 (7.7)	78.7 (1.9)	75.8 (0.9)
b (–)	0.092 (0.006)	0.087 (0.001)	0.19 (0.01)
n (–)	–	5.06 (0.5)	–
a (–)	–	–	43.6 (11)
RMSE (mg g^{-1})	4.8	1.7	1.1
AW (%)	0	4.7	95.3

[a] Parameter standard errors are given in parentheses.

Fig. 1 shows the experimental isotherm for the adsorption of tetracycline hydrochloride onto a laboratory-synthesized porous carbon, designated HC1000–0.075 in the original study [3]. The data were obtained from batch experiments conducted at 25 °C and pH 4.5. In laboratory studies, the hydrochloride salt is often preferred over the base form due to its greater solubility and stability, with a reported solubility of approximately 27,000 mg L^{-1} at 25 °C [42],. This solubility value was used to convert the original q versus c data into the q versus c/c_s format shown in panels a and b of Fig. 1.

As shown in Fig. 1, the experimental isotherm spans a narrow c/c_s range of 0–0.0025, with an apparent plateau near $c/c_s = 0.001$. The implications of this limited concentration range are discussed later. The fits of the DR, DA, and DRM equations to the experimental data are also presented in Fig. 1, with corresponding parameter estimates and fit statistics summarized in Table 2. It is evident that the DA and DRM equations provide better fits than the DR equation. This is further supported by the RMSE values in Table 2, where the DRM equation yields the lowest error, indicating the highest accuracy. The Akaike weight analysis reinforces this finding, assigning a 95.3% likelihood to the DRM model, thereby justifying its use despite the inclusion of three adjustable parameters.

Table 2 shows that all parameters were estimated with acceptable precision, as indicated by the relatively small standard errors. The b values from the DR and DA equations are similar but lower than that from the DRM equation. In contrast, the q_m estimate from the DR equation deviates considerably from those obtained using the DA and DRM equations. To assess the practical relevance of these differences, the q_m estimates are compared with the experimental plateau observed in Fig. 1, approximately 70 mg g^{-1}. The DR, DA, and DRM equations overestimate this value by 54%, 12%, and 8%, respectively. This

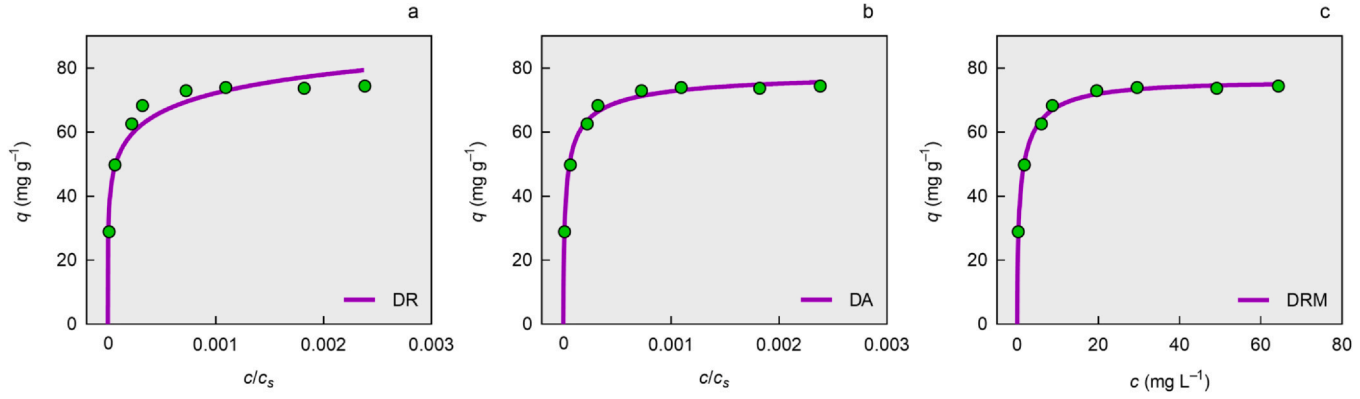

Fig. 1. Equilibrium isotherm for tetracycline hydrochloride adsorption on porous carbon [3]. Solid lines represent model fits using (a) the DR equation, (b) the DA equation, and (c) the DRM equation.

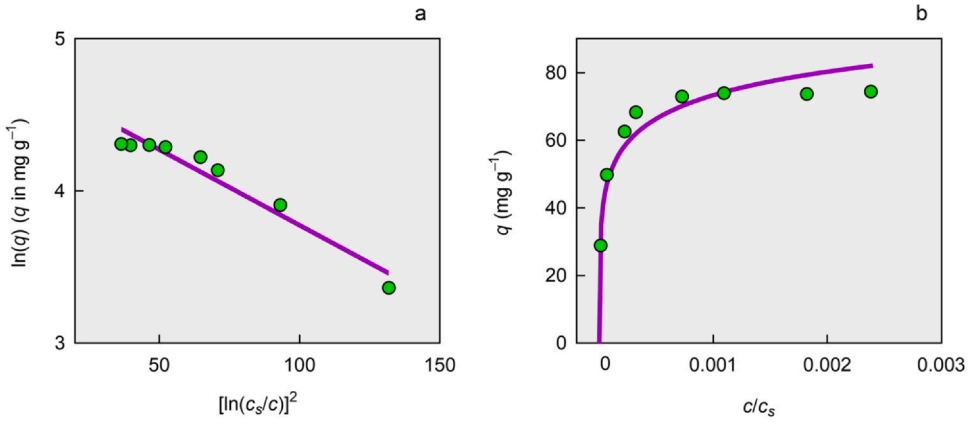

Fig. 2. (a) Linearized DR plot (Eq. (2)) fitted to tetracycline hydrochloride adsorption data. (b) Corresponding q versus c/c_s curve generated using the DR equation (Eq. (1)) with parameters estimated from panel (a).

comparison indicates that the DRM equation provides the most accurate prediction of q_m. Significant overestimation of q_m can be problematic in practical applications, as it may lead to unrealistic expectations of adsorption performance and suboptimal design of treatment systems.

Achieving a good fit of the DA equation to the experimental data requires an n value of 5.06, as shown in Table 2. Constraining $n = 2$, which effectively reduces the DA equation to the DR form, results in a significantly poorer fit. While this simplification historically enabled the use of linear characteristic curves, numerous studies have demonstrated that many experimental isotherms cannot be accurately described by the linearized DR equation. The tetracycline hydrochloride isotherm clearly illustrates this limitation. Fig. 2a shows the fit obtained using the linearized DR equation (Eq. (2)), yielding an R^2 value of 0.942. Despite this moderately high value, the transformed data deviate from linearity, highlighting the inadequacy of linear regression in this context. Fig. 2b presents the corresponding q versus c/c_s curve, calculated using the parameter estimates from the linearized DR equation ($q_m = 117.8\ \text{mg g}^{-1}$, $b = 0.1$). This calculated curve results in an RMSE of $5.4\ \text{mg g}^{-1}$, substantially higher than the RMSE of $1.7\ \text{mg g}^{-1}$ obtained from the nonlinear DA fit in Fig. 1b. This discrepancy underscores the limitations of relying on the linearized DR equation for isotherm modeling and questions its continued widespread use in adsorption studies.

In summary, the DR equation is less effective than the DA and DRM equations, as it fails to accurately capture the tetracycline hydrochloride isotherm and yields an overestimated q_m value. To enhance the reliability of adsorption data analysis, researchers are encouraged to move beyond exclusive reliance on the DR equation and consider the DA and DRM models. When the DR equation is applied, it should be evaluated in parallel with the DA or DRM equation to enable a more robust and comprehensive interpretation of equilibrium behavior.

Table 3
Model parameters and fit statistics for metronidazole adsorption on activated carbon [4].[a]

Parameter/fit metric	Isotherm model		
	DR	DA	DRM
q_m (mg g^{-1})	816.8 (20)	630.5 (28)	608.8 (26)
b (–)	0.159 (0.003)	0.146 (0.001)	0.239 (0.03)
n (–)	–	3.41 (0.4)	–
a (–)	–	–	563.2 (273)
RMSE (mg g^{-1})	10.7	6.8	7.2
AW (%)	15.8	53.2	31.0

[a] Parameter standard errors are given in parentheses.

3.1.2. Case 2: adsorption of metronidazole on activated carbon

This case examines the adsorption of metronidazole on activated carbon, as reported by El Farissi et al. [4] (for details, see the Supplementary Material). Metronidazole is a widely used antibiotic and antiprotozoal agent, essential for treating a variety of bacterial and parasitic infections. However, its extensive use in human and veterinary medicine has led to its frequent detection in aquatic environments.

The equilibrium isotherm for metronidazole adsorption was obtained from batch experiments conducted at 20 °C and pH 7 [4]. The activated carbon was synthesized from cistus shells via phosphoric acid activation and fixed-bed pyrolysis [4]. Reported solubility values for metronidazole in water vary: 11,000 mg L^{-1} at 25 °C [4], approximately 7000 mg L^{-1} [43], 9500 mg L^{-1} at 25 °C [44], and about 9000 mg L^{-1} at 22 °C [45]. In the absence of a reported value at 20 °C, the 9000 mg L^{-1}

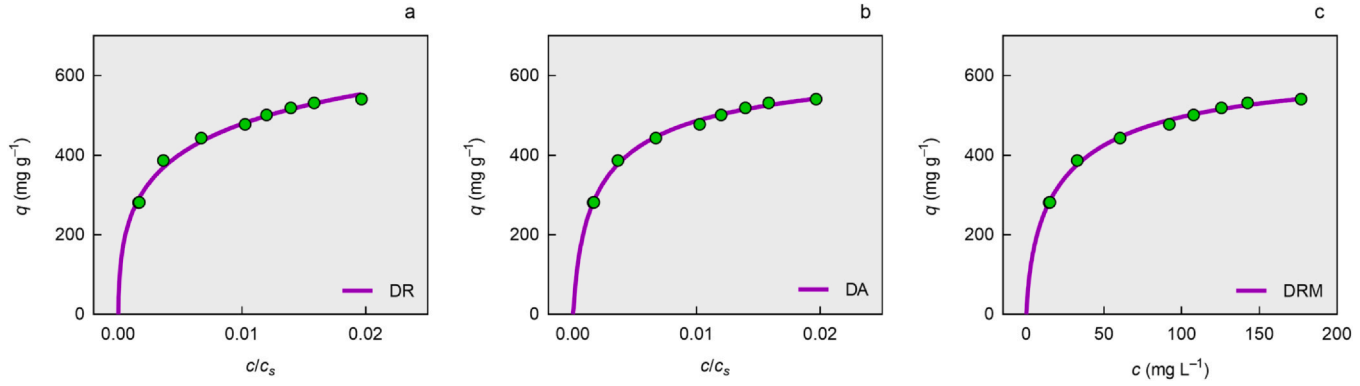

Fig. 3. Equilibrium isotherm for metronidazole adsorption on activated carbon [4]. Solid lines represent model fits using (a) the DR equation, (b) the DA equation, and (c) the DRM equation.

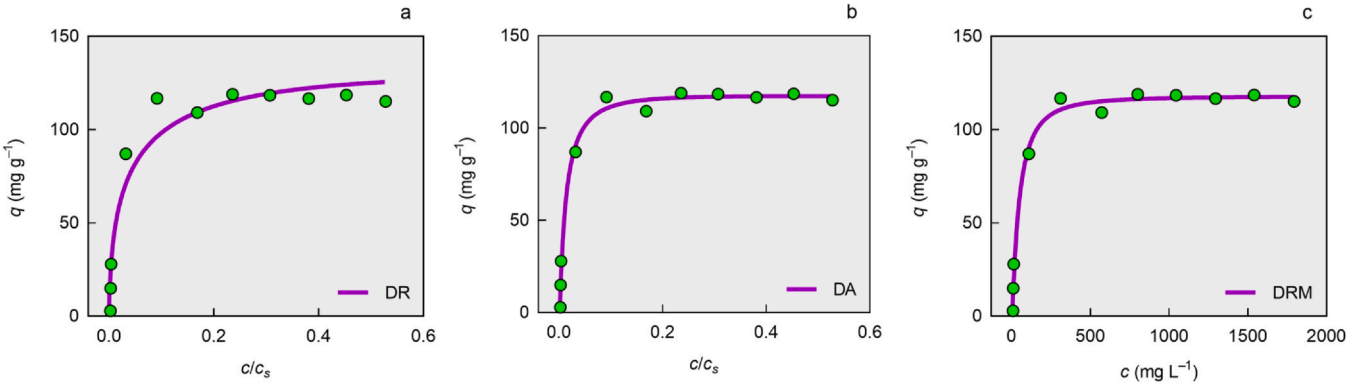

Fig. 4. Equilibrium isotherm for ofloxacin adsorption on clay [1]. Solid lines represents model fits using (a) the DR equation, (b) the DA equation, and (c) the DRM equation.

solubility at 22 °C was adopted. This c_s value remains effectively constant within the pH range of 3–8 [45].

Fig. 3 presents the experimental isotherm for metronidazole adsorption, plotted as q versus c/c_s in panels a and b, using the original q versus c data and a c_s value of 9000 mg L^{-1}. The isotherm spans a c/c_s range of 0–0.02, which is approximately ten times broader than the 0–0.0025 range observed in case 1. As shown in Fig. 3, all three models provide visually satisfactory fits to the data. However, the RMSE values in Table 3 indicate that the DA equation offers the best quantitative fit, slightly outperforming the DRM equation. This result is further supported by the Akaike weight analysis, which assigns a weight of about 53% to the DA equation, compared to 31% for the DRM equation, indicating a modest preference for the former.

Table 3 shows that the b values obtained from the DR and DA equations are similar but lower than that from the DRM equation. In contrast, the q_m estimate from the DR equation is substantially higher than those from the DA and DRM models. As the experimental isotherm does not display a well-defined plateau at high concentrations, the q_m estimates are evaluated against the observed maximum q value of 541.1 mg g^{-1}. The DR equation overestimates this value by 51%, while the DA and DRM equations exceed it by 17% and 13%, respectively. These results indicate that the DA and DRM models not only provide better fits to the data but also produce more realistic q_m estimates.

3.1.3. Case 3: adsorption of ofloxacin on clay

This case focuses on the adsorption of ofloxacin on a commercial clay adsorbent, as reported by Antonelli et al. [1] (see the Supplementary Material for details). Ofloxacin is a broad-spectrum fluoroquinolone antibiotic widely used in human and veterinary medicine to treat bacterial infections. Its extensive use has resulted in its detection in various environmental compartments, including surface water and groundwater, raising concerns about its persistence and potential ecological risks.

Fig. 4 shows the experimental isotherm for ofloxacin adsorption measured at 25 °C, along with the fitted curves for the three models.

Table 4
Model parameters and fit statistics for ofloxacin adsorption on clay [1].[a]

Parameter/fit metric	Isotherm model		
	DR	DA	DRM
q_m (mg g^{-1})	128.1 (5.7)	117.4 (2.4)	117.9 (2.5)
b (–)	0.224 (0.02)	0.209 (0.006)	0.478 (0.08)
n (–)	–	4.06 (0.5)	–
a (–)	–	–	214.2 (98)
RMSE (mg g^{-1})	12.3	5.6	5.7
AW (%)	0	55.8	44.2

[a] Parameter standard errors are given in parentheses.

Table 5
Effect of the c/c_s range on q_m estimates from the DR, DA, and DRM equations in cases 1–3.

Case	c/c_s range	q_m estimate as a percent of observed maximum q		
		DR	DA	DRM
1	0–0.0025	154	112	108
2	0–0.02	151	117	113
3	0–0.53	109	100	100

The isotherm exhibits a distinct plateau at high concentrations, indicating saturation of the adsorption sites. The aqueous solubility of ofloxacin at 25 °C and pH 7 is 3400 mg L^{-1}, and remains relatively stable between pH 6 and 8 [46]. This solubility value was used to convert the original q versus c data from Antonelli et al. [1] into the q versus c/c_s format shown in panels a and b. The resulting isotherm spans a c/c_s range of 0–0.53, considerably wider than those observed in cases 1 and 2.

The DA and DRM equations offer markedly better fits to the ofloxacin isotherm than the DR equation, as shown in Fig. 4 and supported by the RMSE and AW values in Table 4. As in cases 1 and 2, the b estimates from the DR and DA equations are similar but lower than that from the DRM equation. However, unlike the previous cases, the q_m estimates from all three models are comparable. Specifically, the DR, DA, and DRM equations predict q_m values equivalent to 109%, 100%, and 100% of the observed plateau value of 117.5 mg g^{-1}, respectively.

Table 5 summarizes the influence of the c/c_s range on q_m estimates obtained from the three models across cases 1–3. The results indicate that the DA and DRM equations consistently produce q_m values in good agreement with the observed data, regardless of the c/c_s range. In contrast, the DR equation substantially overestimates q_m when the concentration range is limited—for example, when the maximum c/c_s value is only 0.0025 or 0.02. These findings highlight the importance of using a sufficiently broad c/c_s range to obtain reliable q_m estimates from the DR equation—a condition more readily achieved when the solute has low solubility.

3.2. Type V isotherms

3.2.1. Case 4: adsorption of ciprofloxacin hydrochloride on a nanosorbent

In addition to type I isotherms, the DR, DA, and DRM models are capable of describing type V isotherms. To assess their performance in such cases, two examples of antibiotic adsorption exhibiting type V behavior were selected from the literature. The first example (case 4) involves the adsorption of ciprofloxacin hydrochloride onto magnetic nanoparticles functionalized with seaweed polysaccharides (Fe_3O_4 @ SiO_2/SiλCRG), as reported by Soares et al. [27] (see the Supplementary Material for details). Like ofloxacin in case 3, ciprofloxacin is a broad-

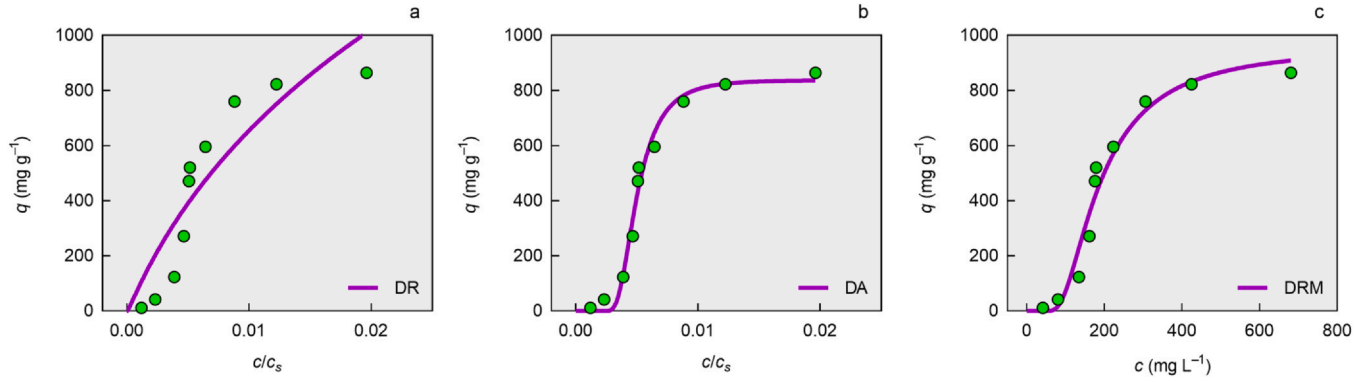

Fig. 5. Equilibrium isotherm for ciprofloxacin hydrochloride adsorption on magnetic nanoparticles [27]. Solid lines represent model fits using (a) the DR equation, (b) the DA equation, and (c) the DRM equation.

Table 6
Model parameters and fit statistics for ciprofloxacin hydrochloride adsorption on magnetic nanoparticles [27].[a]

Parameter/fit metric	Isotherm model		
	DR	DA	DRM
q_m (mg g^{-1})	3233 (1093)	837.5 (34.7)	960.9 (80)
b (–)	0.274 (0.03)	0.186 (0.001)	Non-estimable
n (–)	–	20.49 (3.7)	–
a (–)	–	–	Non-estimable
RMSE (mg g^{-1})	145.5	48.7	70.7
AW (%)	0	97.6	2.4

[a] Parameter standard errors are given in parentheses.

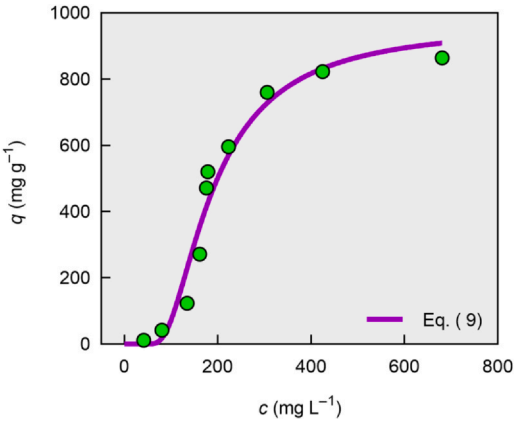

Fig. 6. Equilibrium isotherm for ciprofloxacin hydrochloride adsorption on magnetic nanoparticles [27] fitted with Eq. (9).

spectrum fluoroquinolone antibiotic effective against a wide range of Gram-positive and Gram-negative bacteria.

The equilibrium isotherm for the ciprofloxacin hydrochloride/nanosorbent system was obtained from batch experiments conducted at 25 °C and pH 5. We estimated the solubility of ciprofloxacin hydrochloride at 25 °C to be approximately 34,700 mg L^{-1}, based on a published solubility-temperature plot [42]. This value was used to convert the original q versus c data into the q versus c/c_s format shown in panels a and b of Fig. 5.

As shown in Fig. 5a, the DR equation yields a type I-like curve rather than the expected sigmoidal (type V) profile, resulting in a poor fit to the experimental data. In contrast, the DA and DRM equations accurately capture the sigmoidal shape, as shown in panels b and c. This performance is supported by the RMSE and AW values in Table 6, which identify the DA equation as the most accurate model. Achieving this fit requires an n value of 20.49, far greater than the fixed value of 2 in the DR equation. Table 6 also indicates that unique a and b parameters could not be resolved for the DRM model. While the DA and DRM equations yield q_m estimates consistent with the experimental plateau, the DR equation greatly overestimates q_m at 3233 mg g^{-1}, an implausible value. These findings confirm that the DA equation is the most appropriate model for representing this type V isotherm.

In the original study [27], Soares et al. reported that the DR equation successfully described the sigmoidal profile of the ciprofloxacin hydrochloride isotherm. However, their model, presented as Eq. (9), differs from the standard DR equation defined in Eq. (1). Specifically, Eq. (9) replaces the concentration ratio c_s/c in the logarithmic term of Eq. (1) with $(1 + 1/c)$, thereby eliminating the need for c_s. As shown in Fig. 6, this modified form provides a good fit to the experimental data, yielding $q_m = 961.4$ mg g^{-1}, $b = 161.7$, and RMSE $= 66.2$ mg g^{-1}. However, Eq. (9) represents a mathematically flawed reformulation due to its dimensional inconsistency: the term $1/c$ has units of inverse concentration, rendering the addition of the dimensionless constant "1" invalid [40]. Despite this fundamental flaw, Eq. (9) remains widely used in water contaminant adsorption studies.

$$q = q_m \exp\left\{-\left[b\ln\left(1+\frac{1}{c}\right)\right]^2\right\} \tag{9}$$

A similar modification has been applied to the DA equation, as shown in Eq. (10). This variant has been used to model the adsorption of sulfamethoxazole on activated carbon [18] and ciprofloxacin on various industrial minerals [19]. In these studies [18,19], the issue of dimensional inconsistency was addressed by expressing c in units of grams of solute per gram of solution, making the term $1/c$ dimensionless. However, this adjustment is purely empirical and lacks a sound theoretical basis.

$$q = q_m \exp\left\{-\left[b\ln\left(1+\frac{1}{c}\right)\right]^n\right\} \tag{10}$$

3.2.2. Case 5: adsorption of chlortetracycline hydrochloride on activated sludge

This case examines the adsorption of chlortetracycline hydrochloride onto activated sludge biomass, as reported by Chen et al. [28] (for details, see the Supplementary Material). Chlortetracycline, a broad-spectrum antibiotic in the tetracycline class, is extensively used in veterinary medicine, aquaculture, and animal feed for growth promotion and disease control. The hydrochloride form improves its solubility and stability, allowing for both oral and topical administration. Owing to its widespread use, chlortetracycline enters aquatic environments via agricultural runoff and wastewater discharge.

Fig. 7 shows the type V isotherm for the adsorption of chlortetracycline hydrochloride onto the biosorbent, derived from activated

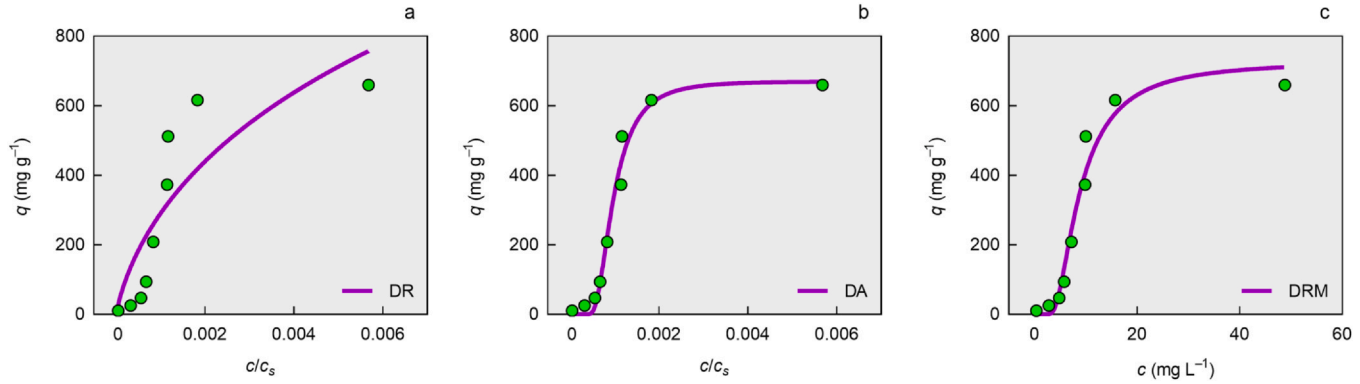

Fig. 7. Equilibrium isotherm for chlortetracycline hydrochloride adsorption on activated sludge [28]. Solid lines represent model fits using (a) the DR equation, (b) the DA equation, and (c) the DRM equation.

Table 7
Model parameters and fit statistics for chlortetracycline hydrochloride adsorption on activated sludge [28].[a]

Parameter/fit metric	Isotherm model		
	DR	DA	DRM
q_m (mg g^{-1})	2571 (1219)	670 (38)	728 (59)
b (–)	0.214 (0.03)	0.142 (0.001)	Non-estimable
n (–)	–	20.46 (3.5)	–
a (–)	–	–	Non-estimable
RMSE (mg g^{-1})	143.6	41.5	56
AW (%)	0	93.7	6.3

[a] Parameter standard errors are given in parentheses.

sludge collected from an aerobic sequencing batch reactor. The isotherm was obtained from batch experiments conducted at room temperature and pH 7.8–8.2. The antibiotic's aqueous solubility, reported as 8600 mg L^{-1} in the original study [28], was used to convert the original q versus c data into the q versus c/c_s format shown in panels a and b of Fig. 7.

The modeling results for this case closely mirror those of case 4. As shown in Fig. 7a, the DR equation fails to capture the sigmoidal shape of the experimental isotherm, instead producing a type I-like curve that deviates markedly from the data. In contrast, panels b and c show that both the DA and DRM equations accurately reproduce the sigmoidal profile, with the DA model providing the best fit and achieving the highest AW score (93.7%; Table 7). The DA equation also offers a significant advantage: unlike the DRM model, it yields unique and well-defined parameter values. The q_m value from the DR equation (2571 mg g^{-1}) substantially overestimates the experimental plateau, whereas the q_m values from the DA and DRM models (Table 7) are consistent with the observed maximum. Taken together, cases 4 and 5 demonstrate the clear superiority of the DA equation for representing type V isotherms.

4. Conclusions

This study demonstrates that while the DR, DA, and DRM equations are mathematically related, their performance in modeling adsorption data differs substantially. Of the three, the DR equation is clearly the least effective, particularly for type I and type V isotherms representing antibiotic adsorption on diverse solid adsorbents. It frequently overestimates maximum adsorption capacities, especially when data are confined to narrow concentration ranges (i.e., small c/c_s values). Its continued use, especially in linearized form, is not justified given its poor accuracy.

Between the DA and DRM equations, the DRM model has practical appeal because it bypasses the need for solubility data. However, it is generally less accurate than the DA equation and presents a major limitation when applied to type V isotherms: some of its parameters cannot be reliably estimated. In contrast, the DA equation consistently offers better fits across both isotherm types and yields robust parameter estimates. We therefore recommend the DA equation as the most reliable and versatile of the three for modeling water contaminant adsorption.

To validate and extend these findings, future studies should examine a wider range of experimental isotherms, especially additional type V isotherms obtained under systematically varied conditions such as pH, temperature, and ionic strength. These factors can significantly influence adsorption behavior and may reveal limitations of the DA equation not evident in the present study. Additionally, resolving parameter nonuniqueness in the DRM equation is critical for extending its applicability. Promising strategies include: (1) collecting more informative data that capture critical regions of type V breakthrough curves; (2) applying global optimization in conjunction with sensitivity and identifiability analysis; (3) reformulating or reparameterizing the DRM model to mitigate parameter correlation; and (4) scaling parameters to enhance numerical stability and reduce nonlinearity. These methodological refinements could strengthen the robustness and broaden the applicability of the DRM equation, particularly in scenarios where solubility data are unavailable or uncertain.

CRediT authorship contribution statement

Ain Aqilah Basirun: Writing – review & editing, Investigation. **Mohd Ali Hashim:** Writing – review & editing, Resources. **Khim Hoong Chu:** Writing – review & editing, Formal analysis, Writing – original draft, 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.

Data availability

The data that support the findings of this study were obtained from previously published articles. These articles are cited within the text and listed in the references section.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.epm.2025.06.001.

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