

Research Article

Removal of Pyrethrin from Aqueous Effluents by Adsorptive Micellar Flocculation

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The equilibrium adsorption of pyrethrin onto aggregates formed by the flocculation of micelles of the surfactant sodium dodecyl sulphate (SDS) with aluminium sulphate is reported. The experimental results were analysed using different adsorption isotherms (Langmuir, Freundlich, Redlich-Peterson, Sips, Radke-Prausnitz, Temkin, linear equilibrium, and the Dubin-Radushkevich isotherms). The Freundlich and linear equilibrium isotherms best describe the adsorption of pyrethrin onto SDS micellar flocs, with the Freundlich adsorption constant, K_F , and the mass distribution coefficient, K_D , of $64.266 ((\text{mg/g})(\text{L/mg})^{1/n})$ and 119.65 L/g , respectively. Applicability of the Freundlich adsorption model suggests that heterogeneous surface adsorption affects the adsorption. The mean free energy value estimated using the Dubinin-Radushkevich isotherm was 0.136 kJ/mol indicating that physisorption may be predominant in the adsorption process.

1. Introduction

Pesticides may cause acute and chronic toxicity problems in aquatic environments and sometimes even entire food chains. There is therefore mounting pressure to minimise, at source, the upstream discharge of pesticides from manufacturing facilities. This requires the use of innovative and efficient methods for the removal and recycling of pesticides from aqueous effluent streams at pesticide manufacturing facilities before discharge into sewers and other receiving water bodies. A promising technology involves the adsorption of small molecules onto micellar aggregates which are formed when Al^{3+} cations interact with sodium dodecyl sulphate (SDS) micelles to form cylindrical to worm-like aggregates [1, 2]. These aggregates form quickly and usually integrate all the micellar surfactant into one single floc which may float on top of the solution and can be easily filtered [3]. The aggregate resulting from flocculation adsorbs organic compounds from the solution it forms in [4], allowing the removal of small molecules by filtration instead of expensive membrane separations. Microscopic photography and X-ray diffractometry

have shown that the aggregates consist of small fragments of liquid crystal dispersed in an amorphous matrix [5]. Organic pollutants bind to the floc by electrostatic attraction as free ions (e.g., phenoxide and benzoate ions) on spots on the floc with local positive charge [6]. Micellar flocculation may also involve the formation of complexes since large cationic complexes may be expected within the Stern layer due to the high Al^{3+} concentration [7].

One of the widely used pesticides is pyrethrin which is commonly used in horticulture for pest control and management. Pyrethrin and pyrethroids such as cypermethrin are also routinely intensively used at very low concentration levels (microgram per litre range) and short periods of time (approximately one hour) in finfish and salmon aquaculture to control sea lice [8, 9]. At high concentration levels pyrethrins are extremely toxic to fish [10]. The release of pyrethrins to the marine environment is suspected to present a definite risk to pelagic and benthic organisms [11]. Prior to their breakdown pyrethrins are toxic to birds, fish, wasps, and other beneficial insects [12]. There is therefore a need to recover pyrethrin from pyrethrin producing industry

TABLE 1: Dependence of mass of micellar floc generated, residual pyrethrin equilibrium concentration, and equilibrium amount of pyrethrin adsorbed onto micellar floc on the initial concentration of aluminium sulphate and SDS solutions.

Molar concentration of solutions of aluminium sulphate (same for the SDS solution) used for the generation of micellar flocs	Mass of micellar floc generated, mg	Residual pyrethrin equilibrium concentration, mg/L	Equilibrium amount of pyrethrin adsorbed onto micellar floc (calculated from mass balance), mg/g
0.01	34.02	50.1	6612.287
0.02	42.53	43.6	5365.624
0.03	53.16	35.1	4372.649
0.04	66.45	34	3506.396
0.05	83.07	30.12	2828.217
0.06	103.83	19.89	2312
0.07	129.79	15.44	1866.708
0.08	162.24	9.48	1511.711
0.09	202.8	9.27	1209.887
0.1	253.5	8.97	968.501

wastewaters before discharge into the marine environment and municipal sewers.

We have investigated the equilibrium adsorption of pyrethrin onto aggregates formed by the flocculation of micelles of the surfactant sodium dodecyl sulphate (SDS) with aluminium sulphate. Eight isotherm models were used to interpret the experimental data.

2. Materials and Methods

2.1. Cleaning of Glassware and Plasticware. All glassware was washed with phosphate-free detergent and rinsed with tap water, then rinsed with 10% hydrochloric acid, and finally rinsed four times with deionised water.

2.2. Reagents. Aluminium sulphate (AR grade), 70% sodium lauryl sulphate, sodium hydroxide, and hydrochloric acid were purchased from a local supplier, Associated Chemicals Limited, Zimbabwe. Pyrethrin was supplied by Agricura (Pvt) Ltd, Zimbabwe. A color standard solution (500 platinum-cobalt units) was used to standardize the Hach DR/2010 Spectrophotometer. All chemicals were used without further purification.

2.3. Stock Solutions. Stock solutions of the various reagents (surfactant, aluminium sulphate, acid, and alkali) were prepared and kept at 25°C. Working solutions were made by making the relevant dilutions of the stock solutions with distilled water. A pH value of 3.7 was maintained for all solutions. The pH was not buffered in order to prevent interference of the buffer system with the flocculation process. All experiments were conducted at ambient temperature (26°C) which was above the Kraft point for SDS micelles (25°C) below which the SDS precipitates from solution.

2.4. Flocculation of Micelles and Adsorption of Pyrethrin. Each working solution for aluminium sulphate was initially dosed with 1000 ppm pyrethrin before commencement of the flocculation of micelles. To initiate the flocculation and adsorption process 250 mL of aluminium sulphate solution of a known concentration doped with 1000 ppm pyrethrin was mixed with an equal volume of surfactant of the same concentration as the aluminium sulphate solution in a 1000 mL beaker and stirred with a magnetic stirrer at 300 rpm. Small portions of the mixture were withdrawn at time intervals, filtered using a 45 µm Whatman cellulose nitrate membrane, and analysed for residual pyrethrin using a HACH DR/2010 Spectrophotometer. The amount of pyrethrin adsorbed by the micellar flocs at equilibrium was calculated by mass balance (see Table 1) as

$$q_e = \frac{(C_0 - C_e)V}{W}, \quad (1)$$

where C_0 and C_e are the initial and equilibrium pyrethrin concentration (mg/L), V is the volume of solution (L), and W is the mass of the micellar floc (g).

2.5. Sample Analysis. A HACH DR/2010 Spectrophotometer was used to indirectly measure the concentration of pyrethrin in samples. The HACH method 8025 based on the APHA platinum-cobalt standard method for water, wastewater, and seawater [13] was used to provide indirect measurements of pyrethrin concentrations using a calibrated curve relating Pt-Co units to pyrethrin concentration. In brief the method entails the determination of color by entering the Hach DR/2010 stored program number of 120 and adjusting the wavelength to 455 nm. The instrument is zeroed with a blank solution and then standardised with a standard solution of known Pt-Co units. After the instrument is standardized it is then used to record Pt-Co units for the different sample

solutions and converting these Pt-Co units to pyrethrin concentrations using a calibrated curve.

From Table 1 it can be seen that the residual solute concentration decreases with the amount of micellar floc generated.

2.6. Equilibrium Adsorption Isotherms. The experimental results were analysed using different adsorption isotherms (Langmuir, Freundlich, Redlich-Peterson, Sips, Radke-Prausnitz, Temkin, linear equilibrium, and the Dubin-Radushkevich isotherms) [14].

2.7. Langmuir Isotherm. The Langmuir isotherm [15] describes homogeneous monolayer adsorption. It assumes that forces of interaction between adsorbed molecules are negligible and that adsorption sites are energetically equivalent and that no further adsorption takes place once an adsorption site is occupied. The model is represented by

$$q_e = \frac{q_m b C_e}{1 + b C_e}, \quad (2)$$

where q_e is the amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g), C_e is the equilibrium concentration of solute in the bulk phase (mg/L), q_m is the maximum adsorption capacity (mg/g), and b is a constant related to the free energy of adsorption (L/mg).

2.8. Freundlich Isotherm. The Freundlich isotherm model [16] was applied to study the biosorption behavior assuming a heterogeneous adsorption on the adsorbent surface and assumes a logarithmic decrease in the enthalpy of adsorption with an increase in the fraction of occupied sites and its equation is

$$q_e = K_F C_e^{1/n}. \quad (3)$$

The Freundlich constants K_F ((mg/g)(L/mg)^{1/n}) and n (dimensionless) are related to adsorption capacity and intensity, respectively.

2.9. Redlich-Peterson Isotherm. The Redlich-Peterson model [17] has features of both the Langmuir and Freundlich isotherms and contains three parameters:

$$q_e = \frac{A C_e}{1 + B C_e^g}, \quad (4)$$

where A , B , and g ($0 < g < 1$) are the isotherm constants.

2.10. Sips or the Langmuir-Freundlich Isotherm. The Sips isotherm [18] is a semiempirical isotherm which reduces to the Freundlich isotherm at high adsorbate concentrations and the Langmuir isotherm at low adsorbate concentrations and its equation is

$$q_e = \frac{q_m b_S C_e^{1/n_S}}{1 + b_S C_e^{1/n_S}}. \quad (5)$$

2.11. Radke-Prausnitz Isotherm. The Radke-Prausnitz [19] isotherm contains three parameters and reduces to the Langmuir model for $\alpha_{rp} = 1$ and to the Henry's Law for $\alpha_{rp} = 0$ and is represented by the following equation:

$$q_e = \frac{q_m b_{rp} C_e}{(1 + b_{rp} C_e)^{\alpha_{rp}}}. \quad (6)$$

2.12. Temkin Isotherm. The Temkin isotherm [20] assumes that during the adsorption process the fall in the heat of adsorption is linear rather than logarithmic and is represented by the following equation:

$$q_e = \frac{RT}{b_T} \ln(K_T C_e), \quad (7)$$

where b_T indicates the adsorption potential of the adsorbent (J/mol) and K_T is the equilibrium binding constant (L/mg).

2.13. Linear Equilibrium Isotherm. Consider

$$q_e = K_D C_e, \quad (8)$$

where K_D is the mass distribution coefficient, q_e is the adsorption capacity (mg/g), and C_e is the pyrethrin concentration at equilibrium (mg/L or ppm).

2.14. Dubinin-Radushkevich (D-R) Isotherm. The Dubinin-Radushkevich (D-R) isotherm [21] is a semiempirical model that was developed to describe adsorption in microporous materials based on the Polanyi potential theory of adsorption [22].

The D-R model is described as

$$q_e = q_m \exp\left(-\beta \left[RT \ln\left(\frac{C_e + 1}{C_e}\right)\right]^2\right), \quad (9)$$

where β is a constant connected with the mean free energy of adsorption per mole of the adsorbate ($\text{mol}^2 \text{kJ}^{-2}$) and q_m is the theoretical saturation capacity (mgg^{-1}). The sorption curve is related to the porous structure of the sorbent.

2.15. Results and Discussion. The adsorption isotherms were fitted to the experimental data using the graphics software *OriginPro 9.1*. The software uses the Levenberg-Marquardt nonlinear curve fitting method [23, 24] which uses two minimization methods: the gradient descent method and the Gauss-Newton method. In the gradient descent method, the sum of the squared errors is reduced by updating the parameters in the direction of the greatest reduction of the least squares objective whilst, in the Gauss-Newton method, the sum of the squared errors is reduced by assuming the least squares function is locally quadratic and finding the minimum of the quadratic. The Levenberg-Marquardt method acts like the gradient-descent method when the parameters are far from their optimal value and acts like the Gauss-Newton method when the parameters are close to their optimal value.

TABLE 2: Summary table of the equilibrium isotherm parameters for the adsorption of pyrethrin onto SDS micellar flocs.

Adsorption isotherm	Isotherm parameters			Coefficient of determination, R^2	Chi-square statistic, $\chi^2 \cdot (10^6)$
Langmuir	q_m (mg/g) 9600	b (L/mg) 0.008		0.137	4.186968
Freundlich	K_F ((mg/g)(L/mg) $^{1/n}$) 64.27	n 0.85		0.973	0.130438
Redlich-Peterson	A 134.93	B 0.08	g 0.42	0.856	0.799945
Sips	q_m (mg/g) 7733.5	b_s 0.075	$g = 1/n_s$ 0.719	0.714	1.585489
Radke-Prausnitz	q_m (mg/g) 2026.6	b_{rp} 0.07	α_{rp} 0.4	0.664	1.863337
Temkin	b_T (J/mol) 0.902	K_T (L/mg) 0.139		0.889	0.536723
Linear		K_D (L/g) 119.65		0.965	0.172125
Dubinin-Radushkevich (D-R)	q_m (mg/g) 6552	β (mol 2 J $^{-2}$) 2.6851×10^{-5}		0.833	0.812780

The adsorption isotherms were not linearised because previously concern has been raised that transformations of nonlinear isotherm equations to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least squares [25]. The best isotherm was adjudged as the isotherm with the highest value of the coefficient of determination, R^2 , and the lowest value of the Chi-square statistic, χ^2 . The value of the Chi-square statistic, χ^2 , is smaller when data from a model are similar to the experimental data and larger when the model data and the experimental data are dissimilar. The isotherm parameters obtained from the nonlinear curve fitting of experimental data to the different isotherms using *OriginPro 9.1* and the corresponding values of the coefficient of determination, R^2 , and the Chi-square statistic, χ^2 , are presented in Table 2.

Based on values of the coefficient of determination, R^2 , and the Chi-square statistic, χ^2 , we note that the Freundlich and linear equilibrium isotherms best describe the adsorption of pyrethrin onto SDS micellar flocs, with the Freundlich adsorption constant, K_F , and the mass distribution coefficient, K_D , of 64.27 ((mg/g)(L/mg) $^{1/n}$) and 119.65 L/g, respectively. The Temkin, Redlich-Peterson, and the Dubinin-Radushkevich isotherms give a fair description of the adsorption of pyrethrin onto SDS micellar flocs, while the Sips and Radke-Prausnitz isotherms give a satisfactory description of the experimental adsorption data. The Langmuir isotherm is inapplicable to describe the experimental adsorption data. The Dubinin-Radushkevich isotherm was used to estimate the adsorption mean free energy E (J/mol) as the sorbate is transferred to the surface of the adsorbent from an infinite distance in the solution. The adsorption

mean free energy was calculated from $E = 1/\sqrt{2\beta}$, so that $E = 136.46$ J/mol. The mean free energy value obtained is less than 20 kJ/mol indicating a possible predominance of physisorption in the adsorption process [26].

2.16. Gibbs Free Energy of Adsorption. The Gibbs free energy of adsorption was calculated from $\Delta G^0 = -RT \ln K_D$, where K_D is the mass distribution coefficient ($K_D = q_e/C_e$, where q_e is the adsorption capacity (mg/g) and C_e is the pyrethrin concentration at equilibrium (mg/L or ppm)). Taking the K_D value that was obtained from the linear equilibrium isotherm, $\Delta G^0 = -11.893$ kJ/mol. The negative value of ΔG^0 confirms the thermodynamic feasibility of the adsorption process and its spontaneity on SDS micellar flocs.

3. Conclusions

The Freundlich and the linear equilibrium isotherms best describe the adsorption of pyrethrin onto SDS micellar flocs with the Freundlich adsorption constant, K_F , and the distribution coefficient, K_D , of 64.266 ((mg/g)(L/mg) $^{1/n}$) and 119.65 L/g, respectively. The value of n was 0.8537, which is between 0 and 10, suggesting relatively strong adsorption of pyrethrin onto the floc. Applicability of the Freundlich adsorption model suggests that heterogeneous surface adsorption affects the adsorption. The mean free energy value estimated using the Dubinin-Radushkevich isotherm was 0.136 kJ/mol indicating that physisorption may be predominant in the adsorption process.

Nomenclature

q_e :	The amount of solute adsorbed per unit weight of adsorbent at equilibrium (mg/g)
q_m :	The theoretical saturation capacity of the adsorbent (mg/g)
K_F :	Freundlich isotherm adsorption constant, (mg/g)(L/mg) ^{1/n}
K_{D^0} :	Mass distribution coefficient, L/g
n :	A dimensionless constant in the Freundlich isotherm related to adsorption intensity
SDS:	Sodium dodecyl sulphate
C_e :	Pyrethrin concentration at equilibrium (mg/L or ppm)
ΔG^0 :	Gibbs free energy of adsorption, kJ/mol
E :	Adsorption mean free energy, J/mol
χ^2 :	Chi-square statistic
R^2 :	Coefficient of determination
β :	A constant in the Dubinin-Radushkevich (D-R) isotherm that is connected with the mean free energy of adsorption per mole of the adsorbate (mol ² J ²)
b :	Langmuir isotherm constant related to the free energy of adsorption (L/mg)
A , B , and g :	Redlich-Peterson isotherm constants
b_S and n_S :	Sips isotherm constants
α_{rp} and b_{rp} :	Radke-Prausnitz isotherm constants
b_T :	Temkin isotherm adsorption potential of the adsorbent (J/mol)
K_T :	Temkin isotherm equilibrium binding constant (L/mg)
R :	Universal gas constant (J/mol·K)
T :	Temperature (K).

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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