



The Relevance of Isotherm and Kinetic Models to Chlorophenols Adsorption: A Review

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Abstract

The derivatives of phenols are among the most widely used chemicals in day-to-day life, which lead to water contamination by chlorophenols (CPs). These compounds belong to a class of those widely used chemicals that increase global concern about environmental protection due to their recalcitrant nature. Adsorption process has been employed for the removal of CPs from contaminated water out of many methods of wastewater treatment. This is due to its insensitivity to toxic substances, effectiveness, universal nature, fast kinetics, as well as the ease of operation and its simplicity in the design and applicability. Thus, this study compared the adsorption isotherm models such as linear and nonlinear and well discussed the fundamental characteristics, modelling, and mathematical derivations. Finally, the study highlighted and addressed the role of different isotherm models that were used in describing the adsorptive removal of CPs using various adsorbents.

Keywords: Chlorophenols, Adsorption, Isotherms, Linear, Nonlinear, Adsorbents

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1. Introduction

The importance of water to life cannot be overemphasized since it serves many other purposes apart from drinking and agriculture (1). A larger fraction of the earth is covered with water. Despite its abundant on the surface of the earth, the World Health Organization (WHO) only recommended a small portion of the fraction to be appropriate for drinking purposes. Even by considering the WHO recommendation, the majority of the populace in developing countries are known for the inadequate supply of hygienic drinking water (2). Natural and artificial activities are among numerous factors that contribute to water pollution which is among the most troubling environmental challenges bedeviling several countries. Water pollution occurs when substances that negatively affect living species contaminate the oceans, rivers, lakes, bays, and streams (3).

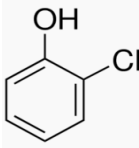
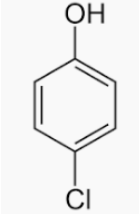
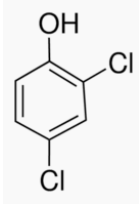
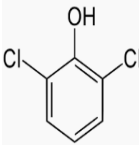
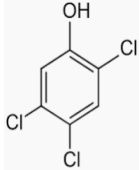
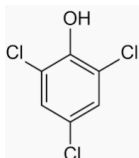
Chlorophenols (CPs) that are covalently bonded to one, two, three, four and/or five chlorine atoms are named as monochlorophenols, dichlorophenols, trichlorophenols, tetrachlorophenols, and/or pentachlorophenols, respectively (4). They are also known as important pollutants, which are widely found in industrial wastewaters and characterized by low biodegradability, strong odour, persistency in the environment, along with carcinogenic and toxic features affecting human and its environment.

Exposure to CPs affects human nervous and respiratory systems and makes them hazardous to health (5-8). Table 1 lists some properties of selected CPs.

The recalcitrant nature of CPs makes them discharge into water bodies as a significant source of pollution. Basically, the accurate data are yet to be known, showing the exact amount of CPs discharged into the environment from various processes. Some of the processes applied for treating wastewater contaminated with CPs include adsorption (9-17), catalytic wet oxidation (18), biodegradation (19), aerobic granular sludge technology (20), anaerobic processes (21), and electrochemical degradation (22). However, Das et al (24) believed that the effectiveness of these technologies in fixing water pollution is questionable with their major threats and drawbacks (Fig. 1).

A recently published review article by Garba et al (16) provided detailed information on CPs, their sources into the environment, classification, and toxicity, and various wastewater treatment methods for their removal. In addition, they described the characteristics of CP adsorption by various adsorbents while not including isotherm and kinetic models. Thus, the objective of this work was to show the relevance of isotherm and kinetic models in studying CP adsorption onto various adsorbents.

Table 1. Selected Properties of Chlorophenols^a

Chlorophenols	Structure	MV ^b (cm ³ /mol)	C _s (g/L)	LogK _{ow}	pK _a
2-chlorophenol		99.8	2.40	2.220	8.50
4-chlorophenol		99.8	2.10	2.418	9.47
2,4-dichlorophenol		111.7	0.47	3.095	8.05
2,6-dichlorophenol		111.7	0.52	2.896	7.02
2,4,5-trichlorophenol		123.7	0.085	3.835	7.10
2,4,6-trichlorophenol		123.7	0.091	3.768	6.59

Abbreviation: MV, molar volume.

^a Properties of chlorophenols were culled from (23) and obtained from SciFinder <https://scifinder.cas.org>.

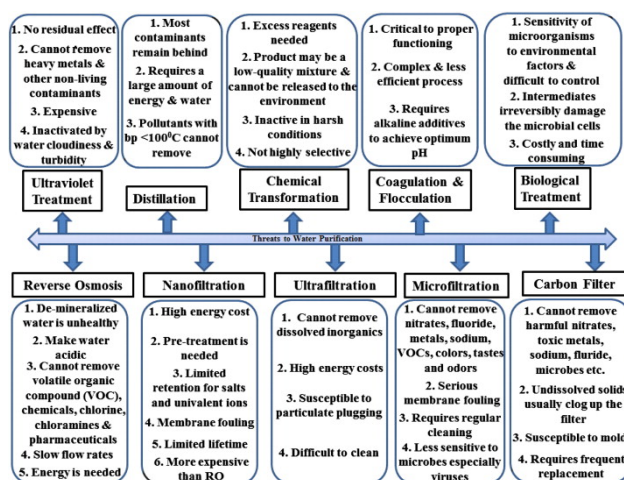


Fig. 1. Some Major Drawbacks Associated With Conventional Water Purification Systems.

Table 2. Adsorption Isotherm Models (47)

Isotherm models	Linear form	Nonlinear form	Plot	Reference
Langmuir	$\frac{1}{q_e} = \frac{1}{K_L Q_a^0 C_e} + \frac{1}{Q_a^0}$ $\frac{C_e}{q_e} = \frac{C_e}{Q_a^0} + \frac{1}{K_L Q_a^0}$ $q_e = -\frac{q_e}{K_L C_e} + Q_a^0$ $\frac{q_e}{C_e} = -K_L q_e + K_L Q_a^0$	$q_e = \frac{K_L Q_a^0 C_e}{1 + K_L C_e}$	$\frac{1}{q_e}$ vs $\frac{1}{C_e}$ $\frac{C_e}{q_e}$ vs C_e q_e vs $\frac{q_e}{C_e}$ $\frac{q_e}{C_e}$ vs q_e	(42)
Freundlich	$\log q_e = \log K_F + \frac{1}{n} \log C_e$	$q_e = K_F C_e^{1/n}$	$\log q_e$ vs $\log C_e$	(48)
Tempkin	$q_e = \frac{RT}{b_T} \ln A_T + \frac{RT}{b_T} \ln C_e$	$q_e = \frac{RT}{b_T} \ln(A_T C_e)$	q_e vs $\ln C_e$	(49)
Dubinin-Radushkevich	$\ln(q_e) = \ln(q_s) - k_{ad} \epsilon^2$	$q_e = (q_s) \exp(-k_{ad} \epsilon^2)$	$\ln(q_e)$ vs ϵ^2	(50)
Flory-Huggins	$\log\left(\frac{\theta}{C_e}\right) = \log(K_{FH}) + n_{FH} \log(1 - \theta)$	$\frac{\theta}{C_o} = K_{FH} (1 - \theta)^{n_{FH}}$	$\log\left(\frac{\theta}{C_o}\right)$ vs $\log(1 - \theta)$	(51)
Hill	$\log\left(\frac{q_e}{q_{SH} - q_e}\right) = n_H \log(C_e) - \log(K_D)$	$q_e = \frac{q_{SH} C_e^{n_H}}{K_D + C_e^{n_H}}$	$\log\left(\frac{q_e}{q_{SH} - q_e}\right)$ vs $\log(C_e)$	(52)
Redlich-Peterson	$\ln\left(K_{RP} \frac{C_e}{q_e} - 1\right) = g \ln(C_e) + \ln(B_{RP})$	$q_e = \frac{K_{RP} C_e}{1 + B_{RP} C_e^g}$	$\ln\left(K_{RP} \frac{C_e}{q_e} - 1\right)$ vs $\ln(C_e)$	(53)
Sips	$\beta_s \ln(C_e) = -\ln\left(\frac{K_s}{q_e}\right) - \ln(a_s)$	$q_e = \frac{K_s C_e^{\beta_s}}{1 + a_s C_e^{\beta_s}}$	$\ln\left(\frac{K_s}{q_e}\right)$ vs $\ln(C_e)$	(54)
Toth	$\ln\left(\frac{q_e}{K_T}\right) = \ln(C_e) - \frac{1}{t} \ln(a_T + C_e)$	$q_e = \frac{K_T C_e}{(a_T + C_e)^{1/t}}$	$\ln\left(\frac{q_e}{K_T}\right)$ vs $\ln(C_e)$	(55)
Koble-Corrigan	$\frac{1}{q_e} = \frac{1}{AC_e^n} + \frac{B}{A}$	$q_e = \frac{AC_e^n}{1 + BC_e^n}$	—	(56)
Polanyi-Manes	$\log q_e = \log Q + a \left(\frac{\epsilon_{sw}}{V_s}\right)^b$	$\epsilon_{sw} = RT \ln\left(\frac{C_s}{C_e}\right)$	—	(57)
Khan	—	$q_e = \frac{q_s b_K C_e}{(1 + b_K C_e)^{\alpha_K}}$	—	(58)
Radke-Prausnitz	—	$q_e = \frac{a_{RPr} \Gamma_R C_e^{\beta R}}{a_{RPr} + \Gamma_R C_e^{\beta R - 1}}$	—	(59)

Table 3. Lists of Error Functions (47)

Error Function	Definition	Abbreviation	Reference
Nonlinear Chi-square test	$\sum_{i=1}^n \frac{(q_{e,calc} - q_{e,meas})^2}{q_{e,meas}}$	χ^2	(70)
The coefficient of determination	$\frac{(q_{e,meas} - q_{e,calc})^2}{\sum (q_{e,meas} - q_{e,calc})^2 + (q_{e,meas} - q_{e,calc})^2}$	R ²	(70)
Sum squares errors	$\sum_{i=1}^n (q_{e,calc} - q_{e,meas})_i^2$	ERRSQ/SSE	(71)
The hybrid fractional error function	$\frac{100}{n-p} \sum_{i=1}^n \left[\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right]$	HYBRID	(72)
Average relative error	$\frac{100}{n-p} \sum_{i=1}^n \left \frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right $	ARE	(73)
Sum of absolute error	$\sum_{i=1}^n q_{e,meas} - q_{e,calc} $	EABS	(74)
Marquardt's percent standard deviation	$100 \sqrt{\frac{1}{n-p} \sum_{i=1}^n \left(\frac{q_{e,meas} - q_{e,calc}}{q_{e,meas}} \right)^2}$	MPSD	(75)
Spearman's correlation coefficient	$1 - \frac{6 \sum_{i=1}^n (q_{e,meas} - q_{e,calc})_i^2}{n(n-1)^2}$	r _s	(70)
Coefficient of non-determination	—	K ₂	(71)
Sum of normalized errors	—	SNE	(76)

Note. q_e : The amount of adsorbate in the adsorbent at equilibrium (mg/g); Q_0^0 : Maximum monolayer coverage capacity (mg/g); C_e : Equilibrium concentration (mg/L); b : Langmuir isotherm constant (dm³/mg); n : Adsorption intensity; T : Temperature (K); K_F : Freundlich isotherm constant (mg/g); R : Universal gas constant (8.314 J/mol K); b_T : Temkin isotherm constant; A_T : Temkin isotherm equilibrium binding constant (L/g); \hat{a} : Dubinin-Radushkevich isotherm constant; Q_s : Theoretical isotherm saturation capacity (mg/g); β : Dubinin-Radushkevich isotherm constant (mol²/kJ²); C_0 : Adsorbate initial concentration (mg/L); θ : The degree of surface coverage; n_{FH} : Flory-Huggins isotherm model exponent; K_{FH} : Flory-Huggins isotherm equilibrium constant (L/g); K_D : Hill constant; n_H : Hill isotherm maximum uptake saturation (mg/L); nH : Hill cooperativity coefficient of the binding interaction; K_{RP} : Redlich-Peterson isotherm constant (L/g); g : Redlich-Peterson isotherm exponent; K_S : Sips isotherm model constant (L/g); \hat{a}_S : Sips isotherm model exponent; K_T : Toth isotherm constant (mg/g); t : Toth isotherm constant' A: Koble-Corrigan isotherm constant (Lnmg¹⁻ⁿ/g); B : Koble-Corrigan isotherm constant (L/mg)n; \hat{a}_{sw} (kJ/mol) is effective adsorption potential; V_x (cm³/mol) is molar volume of adsorbates; a (cm³)^{b+1}/(kg·J^b) and b are fitting parameters; C_s (mg/L) is the solubility of adsorbates; α_K : Khan isotherm model exponent; b_K : Khan isotherm model constant; α_{RP} : Radke-Prausnitz isotherm model constant; I_R : Radke-Prausnitz isotherm model constant; \hat{a}_R : Radke-Prausnitz isotherm model exponent.

2. Adsorption Isotherm Models

Adsorption process is globally proven as the most efficient among various water treatment technologies (25,26) since it possesses very fast kinetics, can be easily handled, and is able to remove high amounts of pollutants (27-29). Establishing the most suitable adsorption system for equilibrium data is very crucial for exploring novel adsorbents for an adsorption process (30) which should be reliable in predicting the correlation between adsorption parameters and quantitatively comparing the behavior of adsorbents for systems (31,32). An equilibrium

relationship, generally known as adsorption isotherms, is the most suitable system since it perfectly describes the interaction between pollutants and the adsorbent materials, thus becoming very vital in optimizing the mechanisms of adsorption processes, expressing the surface properties and the adsorbents capabilities, and designing the adsorption systems effectively (33,34).

Isotherms are used in studying and explaining the whole adsorption and desorption processes. Further, they are considered as functions that relate the adsorbate amount on the adsorbent with its concentration in case of liquid and its pressure if gaseous at a fixed

Table 4. Adsorption Isotherm Models of Chlorophenols Onto Different Adsorbents

Adsorbate	Adsorbent	Isotherm model	Reference
4-Chloroguaiacol	Oil palm shell activated carbon	Langmuir	(78)
4-Chloroguaiacol	<i>Prosopis africana</i> seed hull activated carbon	Langmuir	(68)
2,4,6-Richlorophenol	Loosestrife activated carbon	Temkin	(79)
2,4,6-Trichlorophenol	Cattail fibre-based activated carbon	Freundlich	(80)
2,4,6-Trichlorophenol	Coconut husk-based activated carbon	Langmuir	(81)
2,4,6-Trichlorophenol	Copper (II)-halloysite nanotubes	Freundlich	(82)
2,4,6-Trichlorophenol	Activated carbon from coconut shell	Freundlich	(83)
2,4-Dichlorophenol	Cattail fibre-based activated carbon	Freundlich	(80)
2,4-Dichlorophenol	Organo clays	Langmuir	(84)
2,4-Dichlorophenol	<i>Prosopis africana</i> seed hull activated carbon	Langmuir	(12)
2,4-Dichlorophenol	Single-walled carbon nanotubes	Langmuir	(23)
2,4-Dichlorophenol	Single-walled carbon nanotubes	Polanyi-Manes	(23)
2,6-Dichlorophenol	Modified plantain peel	Freundlich	(85)
4-Chlorophenol	Rattan sawdust based activated carbon	Langmuir	(86)
4-Chlorophenol	Chemically modified chitosan	Freundlich	(87)
4-Chlorophenol	Porous carbon from coconut spathe	Langmuir	(88)
4-Chlorophenol	Nanosized activated carbon	Freundlich	(9)
4-Chlorophenol	Carbon nanofibers	Langmuir	(13)
3-Chlorophenol	Purified multiwalled carbon nanotubes	Langmuir	(89)
3-Chlorophenol	Rice-straw-based carbon	Langmuir	(90)
2-Chlorophenol	Single-walled carbon nanotubes	Polanyi-Manes	(23)

temperature. Generally, adsorption isotherms comprise invaluable curves that depict how the phenomenon of a substance is governed. Such phenomena occur at a fixed pH and temperature where the retention or mobility of such substances moves from aqueous porous media/environments to a solid-phase (35,36). Adsorption equilibrium is the ratio of the amount of substance adsorbed with that remaining in the solution. This is confirmed when the time, in which an adsorbate containing phase is in contact with the adsorbent, is sufficient for the adsorbate concentration in the bulk solution to be in a dynamic balance with the interface concentration (37,38). A graphical representation of the solid-phase against its residual concentration usually depicts the mathematical correlation, which plays a key role in the modeling analysis, the direction of operational design, and the applicable practices of adsorption systems (39). A better perception of the adsorption mechanism is provided by the adsorbent degree of affinity, along with the underlying thermodynamic and their surface properties (40). Over the years, several researchers have reported various equilibrium isotherm models from three different approaches (41). The first reported approach was the kinetic consideration where adsorption equilibrium was assumed to be a state in which both rates of adsorption and desorption are equal (42). Thermodynamic consideration, where a basis for the derivation of various isotherm models was provided in multiple forms, is the reported second approach (43,44). The third approach was called a potential theory which normally conveys the main idea in generating the characteristic curves (45). However, isotherm derivation

from more than one approach is the most fascinating trend in the modeling process, thus leading to the disparity in the physical interpretation of model parameters (46). Table 2 presents various isotherm models based on distinctive assumptions. The assumption with respect to the Langmuir isotherm is monolayer adsorption having a homogeneous surface with a definite number of adsorption sites. On the contrary, the Freundlich model is the most suited model for heterogeneous surfaces and can be applied to multilayer adsorption. In depicting the performance of adsorbents, Langmuir and Freundlich are the most frequently used models for that purpose. Temkin isotherm assumed that a decrease in adsorption heat is linear. Furthermore, Dubinin-Radushkevich isotherm is commonly engaged in determining whether the adsorption mechanism is chemical or physical with a heterogeneous surface hosting free energy. Similarly, the spontaneous and feasibility nature of the adsorption process is regarded as the major assumption associated with Flory-Huggins isotherm. Another important assumption related to Hill isotherm is how the binding sites of a ligand in a macromolecule can influence other binding sites within the same macromolecule. All the aforementioned isotherms are categorized as two-parameter isotherms. The most popular and frequently used three-parameter isotherms are those in the Redlich-Peterson isotherm model. It combines the Langmuir and Freundlich models that can be used over a vast range of concentrations and in both heterogeneous and homogeneous systems. Other three-parameter isotherms include Sips, Koble-Corrigan, Toth, Radke-Prausnitz, and Khan isotherm (47,60).

3. Error Functions

During the analysis of adsorption experimental data, linear and non-linear isotherm models were used to elaborate on the suitability or best fitting of a model(s) to the process (61). This was aimed toward comparing the experimental data and the predicted isotherm owing to obtain a good understanding of the equilibrium state relationship between adsorbent and adsorbate. Due to linear regression models of popularity and simplicity, many researchers prefer to describe the nature of the adsorption isotherm model and select the optimum model of the process having the minimal error between the experimental data and the predicted isotherm (62-64). However, in some studies, researchers emphasized that the use of nonlinear regression models in analyzing the adsorption equilibrium is more accurate in predicting the optimum isotherm for the process (31). Nonetheless, other researchers believed that both linear and nonlinear regression models are suitable for the selection of best-fitted adsorption equilibrium isotherm depending on the manner of application and magnitude of error (61). Moreover, many error functions are employed in model selection in order to determine the nature of error which still relies on the definition of the intended function. This helps in ascertaining those assertions (64-67).

Rahim and Garba compared the validity of five different linear Langmuir isotherm models by incorporating χ^2 since R^2 is no longer reliable when it comes to justifying the basis for selecting the most suitable model of adsorption because it only signifies the fit between the linear forms of isotherm equations and experimental data. Additionally, low χ^2 values signify the best fit and describe the suitability between the predicted and experimental values of the adsorption capacity (68).

In the present study, several mathematically rigorous error functions were applied in addition to the Chi-square, including hybrid fractional error function, the sum of squares errors, the sum of normalized errors, Spearman's correlation coefficient, average relative error, the coefficient of non-determination, and the sum of absolute error Marquardt's percent standard deviation (Table 3). This was done to drastically address and confront the inherent bias resulting from the transformation that leads toward a diverse form of parameter estimation errors and fits distortion (69).

Recently, linear regression has been the most feasible tool among the other instruments for defining the best-fitting relationships (71). In addition, it mathematically analyzes the adsorption systems, quantifies the adsorbates distribution (77), and verifies the consistency and theoretical assumptions of an isotherm model (70). During the development of computer technology in the 1980s, the progression of nonlinear isotherm modeling was broadly facilitated and motivated to be in line with the developing technology (70). In contrast to the model

linearization, nonlinear regression usually involves the maximization or minimization of error distribution between the experimental data and the predicted isotherm based on its convergence criteria (69).

4. Reported Isotherm Models for Chlorophenol Adsorption

The reported adsorption isotherms of some CPs onto different adsorbents are summarized in Table 4.

The functionalization of single-walled carbon nanotubes (SWCNTs) was reported by Ding et al (23), which was applied for CP adsorption from aqueous solution. They indicated that three models well fit the isotherms with the presence of grooves, an external surface, and interstitial channel adsorption sites in the closed-ended bundles of the SWCNT (91). The researchers further revealed that the SWCNT interstitial channels are extremely tiny for the adsorbate molecules to fit into, thus proposing the major adsorption sites to rely on grooves and external surface area (92). As a result, surface adsorption dominates the adsorption process. Considering that the Langmuir model and Polanyi-Manes models were both derived from surface adsorption (57, 93) and the Freundlich model was a special form of Polanyi-Manes model (94), it was reasonable that the adsorption data were well fitted to those three models.

In another development, Ren et al (80) reported Freundlich as the most suitable isotherm model in describing the adsorption of 2,4-dichlorophenol and 2,4,6-trichlorophenol onto cattail fibre-based activated carbon. Their revelation hinted at the uptake of both 2,4-dichlorophenol and 2,4,6-trichlorophenol was multimolecular layer adsorption with interactions between the adsorbed molecules, and the surface of the cattail fibre-based activated carbon was relatively heterogeneous. Additionally, Garba and Rahim (12) studied the adsorptive removal of para-chlorophenol and 2,4-dichlorophenol by employing the activated carbon from *Prosopis africana* seed hulls as the adsorbent. They carried out their experiments at three different temperatures by fitting the experimental data into Langmuir, Freundlich, and Temkin models and reported that the R^2 of the three models was higher than 0.90 for all studied temperatures. However, the applicability of the Langmuir isotherm model became more pronounced compared to the other two isotherms when they applied the chi-square values. The fitness of the Langmuir model to the adsorption process connotes that the two CP molecules from bulk solution were adsorbed on specific monolayer which is homogeneous in nature.

As shown in Table 4, Langmuir and Freundlich were the most important isotherm models in fitting the CP adsorption data with the nature of the adsorbent, as well as the type of CPs playing a significant role in determining whether the process is monolayer or multilayer on a homogeneous or heterogeneous surface, respectively.

5. Adsorption Kinetic Studies

Elovich equation and Lagergren pseudo-first and second order (1 & 2) models are the most popular and widely used models for kinetic study. This facilitates the understanding of the dynamics of an adsorption process.

5.1. Pseudo-first Order Model

The adsorption rate constant is ascertained from the pseudo-first order equation given by (95) as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad (1)$$

Where q_e and q_t are the amount of CPs adsorbed onto the adsorbents (mg g^{-1}) at equilibrium and at time t , respectively, while k_1 is the pseudo-first order rate constant (h^{-1}).

5.2. Pseudo-second Order (1 & 2)

The pseudo-second order equation is expressed in two linear forms (95):

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

$$\frac{1}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) \frac{1}{t} + \frac{1}{q_e} \quad (3)$$

where k_2 ($\text{g mg}^{-1} \text{h}^{-1}$) is the rate constant of the second-order adsorption.

5.3. Elovich Kinetic Model

The primary proposed Elovich equation was to describe the kinetics of gases and chemisorptions on the solids. The model shows a variation in the energy of chemisorptions, which is ascribed to a change in surface coverage or a continuous and specific range of site reactivity. Its linear equation is expressed as (79):

$$q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln t \quad (4)$$

The term $(\frac{1}{b})$ stands for the number of attainable adsorption sites whereas $(\frac{1}{b})\ln(ab)$ denotes the quantity of adsorption $\ln t = 0$. (79).

The examples of the adsorption kinetics of chlorophenols onto different adsorbents are summarized in Table 5.

6. Adsorption Thermodynamics

The adsorption thermodynamics of the CPs are studied to verify the adsorption process spontaneity. The most popular studied thermodynamic parameters are entropy change (ΔS), Gibb's free energy change (ΔG), and enthalpy change (ΔH). The evaluation of the thermodynamic parameters is carried out using Van't Hoff equation which is expressed as:

$$\ln K_D = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (5)$$

where K_D , T , and R represent the distribution coefficient, the absolute temperature (K), and the universal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), respectively. A linear graphical representation is obtained when $\ln K_D$ is plotted against $1/T$ deriving ΔH and ΔS from the slope and intercept, respectively. In this study, ΔG was evaluated from the Gibbs-Helmholtz relation (96-98):

$$\Delta G = -RT \ln K_D \quad (6)$$

Physisorption was revealed to describe the adsorption of phenolic compounds on a water-compatible hypercrosslinked polymeric resin (101), as well as from agro-based derived adsorbents (102). On the other hand, the adsorption of pure phenolics onto activated carbons and polymeric resins (103), modified macroalga (104), as well as viable fungal biomass (105) was described as exothermic based on the obtained ΔH values. Endothermic processes were also reported for the adsorption of pure phenols onto waste leached residue, from manganese production (106), and the vegetal cords (107). The same process was also reported for mixed standard phenols onto activated carbon from the olive husk (108).

Table 5. Adsorption Kinetics of Chlorophenols Onto Different Adsorbents

Adsorbate	Adsorbent	Kinetic model	Reference
4-Chloroguaiacol	Oil palm shell activated carbon	Pseudo-second order	(78)
4-Chloroguaiacol	<i>Prosopis africana</i> seed hull activated carbon	Pseudo-second order	(68)
4-Chloro-2-methoxyphenol	Oil palm shell activated carbon	Pseudo-second order	(2)
2,4,6-Trichlorophenol	Loosestrife activated carbon	Pseudo-second order	(79)
2,4,6-Trichlorophenol	Copper (II)-halloysite	Pseudo-second order	(82)
2,4,6-Trichlorophenol	Chemically modified chitosan	Pseudo-second order	(87)
2,4,6-Trichlorophenol	Cattail fibre-based activated carbon	Pseudo-second order	(80)
2,4-Dichlorophenol	Organo clays	Pseudo-second order	(84)
2,4-Dichlorophenol	Polyimide (PI)-based carbon nanofibers	Pseudo-second order	(99)
2,4-Dichlorophenol	Chemically modified chitosan	Pseudo-second order	(87)
2,6-Dichlorophenol	Modified plantain peel	Pseudo-second order	(85)
4-Chlorophenol	Rattan sawdust based activated carbon	Pseudo-second order	(86)
4-Chlorophenol	Chemically modified chitosan	Pseudo-second order	(87)

7. Conclusion and Future Outlook

In this review, the adsorption process was reported for its attributes in effectiveness, simplicity in design and applicability, fast kinetics, and its universal nature for the removal of CPs from wastewater among the other wastewater treatment methods. A number of adsorbents such as agricultural wastes, active carbons, industrial by-products, biosorbents, and nanomaterials were used at various conditions for the decontamination of wastewater containing CPs. However, in the adsorption system designing, researchers have developed and revealed linear regression as the most preferable option in the last few decades despite indications from recent investigations signaling an increasing discrepancy and shortcoming of the model, which propagates toward a different outcome. Despite the above-mentioned explanations, linearization remains the most trusted option in the literature and statistics prove its application in over 95% of the liquid-phase adsorption systems. Hence, the next real challenge in the adsorption field is the identification and clarification of both isotherm models in various adsorption systems.

Conflict of Interest Disclosures

The authors declare that they have no conflict of interests.

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