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Analysis of adsorption isotherms in wastewater treatment using batch processes

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Abstract

In batch-type adsorption operations, a predetermined quantity of adsorbent is mixed with a fixed volume of contaminated water or a specific solution of adsorbate until the concentration of the contaminant or adsorbate in the aqueous phase meets a specified target level or is completely removed. The amount of adsorbent and the contact duration are adjusted according to the process requirements. After adsorption, the adsorbent may be disposed of or recycled for future use. Factors such as the concentration of adsorbate species, agitation speed, quantity of adsorbent, and particle size significantly influence the time required to achieve equilibrium. Batch adsorption processes typically involve either single-stage or multi-stage counter-current operations. Single-stage operations, suitable for treating small volumes of wastewater, utilize fill-and-draw processes. Multi-stage operations, employed for larger volumes, involve series configurations alternating between fill and treat modes. Powdered adsorbents are commonly used in such processes to enhance surface area and reduce diffusion resistance within pores. Numerous contaminants have been effectively removed using batch techniques in various applications.

Keywords: Batch technique, adsorbate, species, contaminated

1. Introduction

Physical and chemical adsorption are among the most effective techniques used for filtering undesirable substances from wastewater and effluent streams using solid substrates. These processes are integral to the purification of water and wastewater.

Understanding the adsorption isotherm in batch wastewater treatment processes is crucial. It provides standardized methods to assess system feasibility and select appropriate biosorbents. At equilibrium in a solid-liquid system, adsorbate species distribute between the solid-solution interface and the bulk phase at a specific temperature. The maximum amount of adsorbate that can adhere to a solid surface correlates with its concentration at a constant temperature.

The Langmuir isotherm is widely employed to describe adsorption in this context. It postulates monolayer coverage of adsorbate on the biosorbent surface as its fundamental premise.

1.1 Adsorption isotherms

In a solid-liquid system, solute concentration on the solid surface and its adsorption from the solution increase until equilibrium is reached. This dynamic continues until the concentrations of solute on the surface and in the solution reach a balanced state. Equilibrium is influenced by factors such as the nature of the adsorbent, temperature, type of solute, pH, particle size, and other variables. Importantly, equilibrium conditions have been observed to vary with initial solute concentration. The study of adsorption equilibrium is crucial for designing heterogeneous chemical processes and constructing reactors for adsorption-based waste treatment. Adsorption isotherms provide valuable insights into the extent of surface coverage by the adsorbent across different conditions.

Chemical engineers rely on equilibrium and kinetic data to design and optimize adsorption units. Equilibrium data are particularly essential for determining the maximum adsorption capacity of an adsorbent under dynamic

conditions. Researchers have developed mathematical relationships to describe the distribution of adsorbate between the adsorbent and liquid-solid systems at dynamic equilibrium. An adsorption isotherm is a fundamental tool used when temperature remains constant throughout the adsorption process. It establishes a relationship that quantifies how the adsorbate concentration in the solution relates to the adsorbate concentration on the adsorbent's surface at equilibrium. This information is crucial for designing efficient adsorption processes in various applications, from environmental remediation to industrial separations.

1.2 Rate of adsorption

Understanding the kinetics of adsorption is crucial for assessing the feasibility of a process and determining the suitability of an adsorbent for wastewater treatment. The adsorption process at the solid-solution interface typically involves three key mechanisms:

1. Adsorbate species diffuse within the pores of the adsorbent particles.
2. Adsorbate species migrate from the solution to the external surface of the adsorbent particles through the aqueous film surrounding the adsorbent.
3. Adsorbate species bind to sites on the interior surface of the adsorbent particles, including pores and capillary spaces.

Among these mechanisms, the third phase-where adsorbate species adhere to the interior surface of the adsorbent-is rapid and not typically rate-limiting. In contrast, the first and second phases, involving diffusion within pores and migration through the aqueous film, are generally considered rate-limiting steps.

In batch operations with high agitation levels, pore diffusion often becomes the rate-limiting phase due to its influence on the adsorption kinetics. In continuous flow systems, however, film diffusion tends to be the rate-limiting step because of the lower agitation intensity and longer contact times between the adsorbent and the solution.

2. Materials and Methods

The choice of metal ion and biosorbents employed in biosorption processes significantly influences the effectiveness of contaminant removal. Both the rate and capacity of removal are notably affected by these factors. The chemical composition of sorbents varies widely depending on their source, which underscores the importance of their characterization. This characterization is essential for gaining insights into the mechanisms involved in the sorption of Cd(II), Pb(II), and Cr(VI), as the sorption behavior depends on both the sorbate species and the properties of the sorbents. This chapter discusses the origins, concentrations, and toxicity of adsorbates in aqueous systems, emphasizing the outcomes derived from various physico-chemical techniques used to characterize the adsorbents. These techniques are instrumental in elucidating the interactions between the sorbates and sorbents, thereby enhancing our understanding of biosorption processes and their potential applications in environmental remediation.

2.1 Procedure

In order to monitor the progress of adsorption in our experiments, we opted for batch mode operation. This involved shaking 1.0 gram of *Mucor heimalis* and *Spirogyra* sp., chosen as the desired grade adsorbents, with 50 mL of aqueous solutions containing cadmium chloride, lead nitrate, and potassium dichromate at a constant speed of 125 rpm in various glass bottles. Before each experiment, the pH of the adsorbate solution was adjusted using appropriate concentrations of HCl and NaOH. The adsorption process was monitored at regular intervals until saturation was achieved. Following each interval, the concentration of residual adsorbate in the supernatant liquid was determined using an Atomic Absorption Spectrophotometer (Shimadzu AA-6300, Japan) and an Ion Selective Titrator Plus System (Orion Ion Selective Titrator Plus System, Model No. 960, manufactured by Thermo Orion, USA). This methodology allowed us to systematically track the adsorption kinetics of cadmium, lead, and chromium ions onto *Mucor heimalis* and *Spirogyra* sp., providing valuable data for evaluating their effectiveness as biosorbents in water treatment applications. To account for any adsorption on the inside surface of the bottles, blanks were always run without adsorbent under identical concentration, pH, and temperature conditions. However, sorption isotherms were investigated in several glass bottles containing 50 ml of each of the aqueous solutions of Cd (II), Pb (II), and Cr (VI), which were stirred with 1.0 g of various biosorbents until the adsorbate-biosorbent systems in each case reached equilibrium.

3. Results and Discussion

The Langmuir isotherm is employed to visually represent equilibrium data for various systems. Plots of C_e/q_e versus C_e exhibit linear characteristics across all studied systems, indicating the validity of this isotherm within the specified concentration range. Values of Q_0 (maximum adsorption capacity) and b (Langmuir constant) were calculated from the slopes and intercepts of these plots at different temperatures.

The findings reveal that for Cd(II) and Pb(II), using both biosorbents, the adsorption capacity Q_0 decreases with increasing temperature. Conversely, for Cr(VI), the adsorption capacity increases with rising temperature when utilizing either biosorbent. These observations underscore the exothermic and endothermic nature of the respective adsorption processes. In endothermic processes, Q_0 values tend to increase with temperature, aligning well with previously published studies. Conversely, in exothermic processes, Q_0 values decrease with temperature, consistent with findings reported by other researchers.

The equilibrium parameter or separation factor R_L of the Langmuir isotherm is described by the relation:

$$R_L = 1 + bC_0$$

Where,

- R_L is the separation factor,
- b is the Langmuir constant,
- C_0 is the initial concentration of the adsorbate in the solution.

This parameter provides valuable insights into the favorability of adsorption processes and can be used to predict whether adsorption is favorable ($0 < R_L < 10 < R_L < 10 < R_L < 1$), unfavorable ($R_L > 1$), or irreversible ($R_L = 0$).

Table 1: R_L values and type of reaction

R_L Values	Type of Reaction
$R_L > 1$	Unfavorable
$R_L = 1$	Linear
$0 < R_L < 1$	Favourable
$R_L = 0$	Irreversible

In the current study, the equilibrium parameter R_L values, presented in Tables 2–4, range from 0 to 1, indicating that the adsorption process was favourable and that the

Langmuir isotherm effectively describes the adsorption behavior. Here, C_0 (mg L^{-1}) represents the initial adsorbate concentration, and b (L mg^{-1}) denotes the Langmuir constant.

The enthalpy of adsorption (H) can be calculated using the Langmuir constant b . Additionally, the Langmuir constant Q_0 , which represents the adsorption capacity, is used to determine the specific surface area S_i . Specific surface area refers to the portion of the total surface area available for adsorption.

These parameters and constants play crucial roles in understanding and quantifying the adsorption process, providing insights into the efficiency and applicability of adsorbents in wastewater treatment and environmental remediation applications.

Table 2: Langmuir constants and separation factor for Cd (ii) of various biosorbents at different temperatures

Biosorbent	Adsorbate	Temp. °C	Langmuir Constants		R_L
			Q^0 (mgg^{-1})	b (lmg^{-1})	
Mucor heimalis	Cd (II)	20	80.10	39.01	1.680×10^{-2}
		30	76.70	27.95	1.926×10^{-2}
		40	74.25	13.75	4.624×10^{-2}
Spirogyra sp.	Cd (II)	20	77.15	34.17	1.914×10^{-2}
		30	74.30	22.43	2.886×10^{-2}
		40	72.05	12.62	5.015×10^{-2}

Table 3: Langmuir constants and separation factor for Pb (ii) of various biosorbents at different temperatures

Biosorbent	Adsorbate	Temp. °C	Langmuir Constants		R_L
			Q^0 (mgg^{-1})	b (lmg^{-1})	
Mucor heimalis	Pb (II)	20	39.25	3.644	4.374×10^{-2}
		30	38.55	2.029	7.591×10^{-2}
		40	37.75	1.263	11.646×10^{-2}
Spirogyra sp.	Pb (II)	20	38.75	2.871	5.487×10^{-2}
		30	38.05	1.962	7.829×10^{-2}
		40	37.20	1.200	12.195×10^{-2}

Table 4: Langmuir constants and separation factor for Cr (vi) of various biosorbents at different temperatures

Biosorbent	Adsorbate	Temp. °C	Langmuir Constants		R_L
			Q^0 (mgg^{-1})	b (lmg^{-1})	
Mucor heimalis	Cr (VI)	20	102.20	11.51	4.163×10^{-2}
		30	107.70	18.57	2.622×10^{-2}
		40	111.10	30.00	1.639×10^{-2}
Spirogyra sp.	Cr (VI)	20	100.00	7.143	6.542×10^{-2}
		30	105.80	9.450	5.025×10^{-2}
		40	109.20	16.65	2.915×10^{-2}

The Langmuir adsorption isotherm operates under the assumption that maximum adsorption occurs when a saturation monolayer of adsorbate species covers the surface of the biosorbent. The Langmuir constant, which relates to the apparent heat change or net enthalpy (H) of adsorption, forms the basis of this application. By taking the logarithm of both sides of the Langmuir equation, the relationship can be transformed into a linear form, facilitating easier analysis and interpretation of equilibrium data. Equilibrium data are invaluable for designing efficient water

treatment plants that adhere to a low-input, high-output policy. Comparative studies on the adsorption capacities of different biosorbents can assist public health engineers in selecting the most suitable biosorbent for achieving maximum contaminant removal. These insights, as presented in this chapter and derived from the aforementioned studies, hold significant importance for environmentalists and technologists alike, contributing to advancements in environmental remediation strategies and sustainable water management practices.

Table 5: Apparent heat of adsorption for saturation coverage of adsorbate ions calculated from langmuir adsorption isotherm of different temperatures.

Adsorbate	Biosorbent	Apparent heat of adsorption (ΔH) (kcal mol ⁻¹)
Cd (II)	Mucor heimalis	-9.420
	Spirogyra sp.	-8.987
Pb (II)	Mucor heimalis	-8.972
	Spirogyra sp.	-8.058
Cr (VI)	Mucor heimalis	8.661
	Spirogyra sp.	7.668

4. Conclusion

Environmental protection encompasses a systematic approach aimed at safeguarding water quality for human consumption, ensuring breathable air, and preserving land integrity. Its objectives are threefold: first, to shield individuals from harmful organisms, toxic substances, and excessive physical forces; second, to prevent environmental conditions that could cause discomfort, irritation, or suffering; and third, to maintain ecological balance and conserve natural resources on Earth.

In industrialized nations, organized efforts to combat environmental pollution trace back to the 19th century, beginning with municipal services such as water supply, sewage management, street cleaning, and solid waste collection. Over time, these efforts expanded to include advanced sewage treatment and waste disposal methods such as landfilling, incineration, and regulated ocean dumping to meet growing demands. Today, environmental protection is firmly institutionalized across most national governments, with ongoing support and reinforcement. Pollution sources are increasingly managed, leading to improvements in waterways, air quality, and waste management practices. Globally, measures to reduce air pollutants like carbon monoxide, hydrocarbons, and particulates have shown significant progress. State-level environmental agencies in many countries have been strengthened to oversee these initiatives.

This study specifically investigates the adsorption isotherm, focusing on how temperature influences the sorption of Cd(II), Pb(II), and Cr(VI). It reveals that increasing temperature tends to reduce both the extent and rate of Cd(II) and Pb(II) adsorption, while enhancing the removal of Cr(VI) through adsorption. Interestingly, temperature does not affect the equilibrium period. The equilibrium data for various adsorbent-adsorbate systems generally fit well with the Langmuir model, highlighting its utility in predicting and understanding adsorption behaviors under different conditions.

5. References

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