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# Physicochemical Principles of Adsorption in Pharmaceutical Systems and Drug Delivery Applications

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**Abstract** **Review Article**

The phenomenon of adsorption is a basic physicochemical behavior that controls molecular interactions at the interfaces in pharmaceutical formulations. From a physicochemical point of view, it has an impact on drug–drug, drug–excipients or drug–carriers' interactions and with the biological surfaces provoking effects such as enhanced loading efficiency of the drug to the delivery system, improved stability of formulations for topical applications (prevents substance migration), dissolution properties (bioavailability enhancement) and therapeutic efficacy. In the pharmaceutical industry, adsorption is connected with fundamental processes like controlled drug liberation, surface-mediated transport and interactions with proteins and cell membranes. Surface properties, molecular structure, thermodynamic driving forces and adsorption kinetics determine the reaction pathways. This review delivers a specific mechanistic overview of the mechanism of adsorption process in pharmaceutical systems by integrating physical chemical principles, and adsorption isotherms as well as the kinetic and thermodynamic models related to drug delivery. Special emphasis is given to adsorption-based delivery systems and adsorption occurring at biological interfaces, demonstrating how fine tuning of the adsorption process enables rational formulation design, increases therapeutic efficacy, and minimizes unwanted interactions.

**Keywords:** physicochemical principles, pharmaceutical systems, adsorption kinetics, drug delivery, interfacial adsorption.



## 1. INTRODUCTION

Pharmaceutical sciences use concepts from chemistry, physics, biology and engineering to investigate drug molecules' behaviour in complex systems. Adsorption is a dominant among physicochemical processes affected on drug performance as it determines molecular interactions at pharmaceutical interfaces [1]. Adsorption influences how drug molecules come into contact with solid carriers, excipients, packaging materials and biological surfaces via surface mediated interactions, which has a direct influence on stability, bioavailability and therapeutic efficacy of drugs. The predominating adsorption paths at these interfaces are depicted in Figure 1. From the physicochemical perspective, adsorption occurs due to intermolecular forces between the adsorbates and adsorbent surface interactions, such as hydrogen bonding, electrostatic attraction, van der Waals force and hydrophobic effects. The contribution of these interactions relative to each other is determined by the molecular structure, surface energy and physicochemical properties of interacting phases [2]. Among pharmaceutical uses, these interactions are purposely used to modulate drug loading and release behaviour and to drive targeted delivery mechanisms [3].

Adsorption phenomena are common to many pharmaceutical dosage forms such as solids, suspensions, emulsions and nanocarrier-based formulations. Adsorption plays a role in the distribution of drug molecules onto excipient and carrier surfaces, which in its turn influences dissolution profiles, formulation stability and the ultimate in vivo performance [4]. In addition, adsorption at biological interfaces, such as plasma proteins and cell membranes is also one of the critical factors, which will determine both pharmacokinetic behavior and biodistribution patterns [5]. Although adsorption is a well-understood phenomenon, it continues to be empirically treated in pharmaceutical development and therefore provides only limited predictive power for drug product formulation. Accordingly, a more fundamental physicochemical

mechanistic insight is required to rationalize the experimental results and develop formulations in a controlled manner. In the scope of this review, we combine physicochemical adsorption models with pharmaceutical formulation aspects to give a consolidated mechanistic framework of the adsorption-controlled drug delivery and therapeutic efficacy.

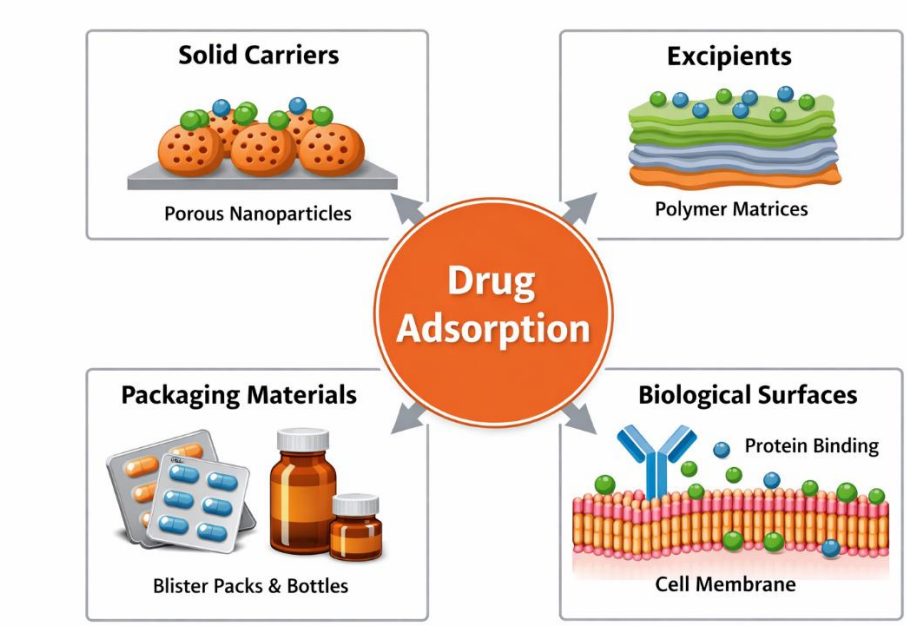


**Figure 1: Schematic illustration of major adsorption processes at pharmaceutical interfaces, including drug adsorption onto biological surfaces, excipients, solid carriers, and packaging materials.**

## 2. Physicochemical Fundamentals of Adsorption

Possible mechanism of the process the term adsorption is defined as the accumulation of molecules at an interface between two different phases due to physical or physicochemical interactions between an adsorbate and the surface of the adsorbent [6]. In pharmaceutical systems the adsorbate is a medicament and the adsorbent can be an inert material, or a porous support or a biological surface. According to the type and intensity of interactions queen, adsorption processes are usually distinguished as physisorption or chemisorption. Physisorption is the result of physical interactions between molecules and has weak intermolecular forces, but is an easily reversible process, which makes it highly relevant for controlled release drugs [7]. In comparison, chemisorption is characterized by much stronger interactions that can be accompanied by partial electron sharing or uphill transfer and which in some cases lead to irreversible adsorption. Surface properties and surface non-homogeneity have great impact on adsorption behaviour in pharmaceutical systems. Adjuvants and vehicle materials often have heterogeneous surfaces, which include adsorption sites with various energies. Such heterogeneity results in nonidentical adsorption energies, which affect loading capacity as well as the surface affinity and release kinetics of drug [8]. The equilibrium state of drug adsorption on homogenous or heterogeneous surfaces is frequently thus modeled using adsorption isotherms.

## 3. Adsorption Isotherms and Modeling in Pharmaceutical Drug–Carrier Systems

Isotherm models of adsorption are commonly used to explain the correlation between drug adsorption on a carrier's surface and the equilibrium concentration in a pharmaceutical system [9]. These models give an indication of surface affinity, adsorption capacity and type of drug-carrier interaction [10]. The Langmuir isotherm, which is based on the monolayer adsorption of adsorbate on homogeneous surface, has been used to describe the drug loading in porous carriers such as silica nanoparticles and polymeric matrices (the good accordance between the model and experimental results shows that accessible adsorption sites for drugs would be uniform and thus release behavior would be predictable) [11]. On the other hand, heterogeneous surface adsorption is expressed by the Freundlich isotherm, and has been used in adsorption on pharmaceutical excipients, polymeric carriers, and biological surfaces with non-uniform adsorption energies [12]. More sophisticated models such as the Temkin and the Dubinin–Radushkevich provide further mechanistic insight by taking into account adsorbate–adsorbate interactions, and distinguishing physical from chemical adsorption mechanisms [13]. Thus, the proper selection and interpretation of adsorption isotherms are important for formulation design; otherwise, a wrong modeling could provide misleading information about adsorption behavior and thermodynamic properties [14].

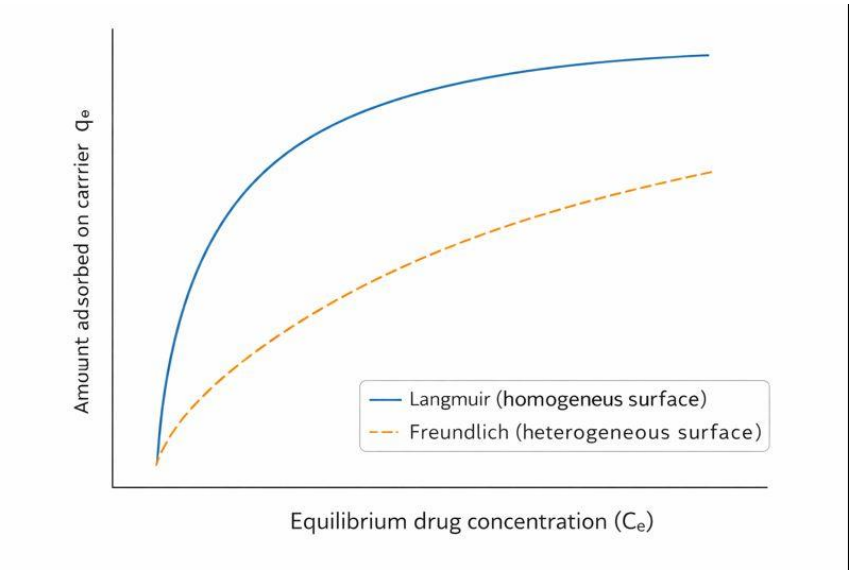


**Figure 2: Conceptual illustration of adsorption phenomena on homogeneous and heterogeneous pharmaceutical carrier surfaces.**

## 4. Thermodynamics and Kinetics of Adsorption

Thermodynamic and kinetic studies are indispensable for understanding the possibility, mechanism, and rate of the adsorption process in pharmaceutical systems. The adsorption behavior can be evaluated based on thermodynamic parameters such as Gibbs free energy, changes in entropy and enthalpy [15]. The negative ΔG indicates the spontaneous nature of the adsorption process at the studied conditions; so drug loading can be successfully produced on the surface of carriers in absence of external energy [16]. Adsorption mechanism can also be inferred from enthalpy change, lower for physisorption and higher for chemisorption. Entropy changes correspond to the difference in interfacial disorder during adsorption, which typically results from displacement of solvent molecules at the adsorbent surface and depends largely on this factor for driving forces of adsorption [17]. Figure 3 depicts the interplay of thermodynamic viability and adsorption courses that determine drug–carrier alignments.

Thermodynamic assessment is supported by kinetic analysis which provides the rate of achieving adsorbent equilibrium [18]. Pseudo-first-order and pseudo-second-order models are typically used in the pharmaceutical systems, but in most cases, the pseudo-second-order model better predicts adsorption behavior owing to prevailing share of surface-related interactions [19]. Diffusion-type models including the intraparticle diffusion model are particularly important for porous supports because they differentiate between a transport limited by particle surface adsorption and that which is controlled by diffusion into the porosities of the support. These differences are important for the rational design of sustained release drug delivery systems as for estimating the drug release in a adsorption-controlled system [20, 21].

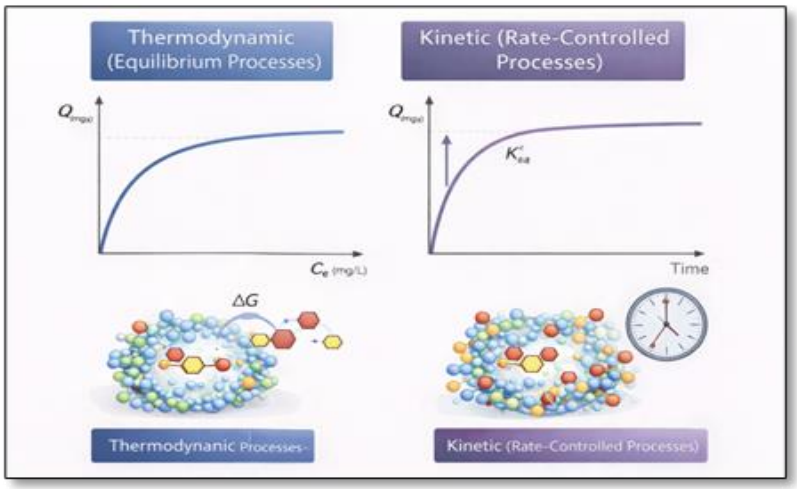


**Figure 3: Conceptual illustration of drug adsorption on pharmaceutical carriers, highlighting thermodynamic and kinetic processes (authors' illustration).**

## 5. Adsorption at Biological Interfaces: Physicochemical Considerations with Pharmaceutical Relevance

The adsorption at biological interfaces is one of the important parts in the interaction between pharmaceutical systems and living bodies. From a physicochemical point of view, biological interfaces such as plasma proteins, cell membranes, and extracellular matrices behave like dynamic adsorption sites that significantly affect the distribution of drugs, their efficacy and more in general drug behavior [22].

### 5.1 Drug–Protein Adsorption

Plasma proteins are the major biological adsorption surfaces that drugs will be exposed to after its administration. Adsorption of drugs onto the serum proteins is governed by their physicochemical properties such as size, shape and charge distribution, hydrophilicity/hydrophobicity, and the presence of particular surface groups [23]. These interactions are mainly driven by noncovalent forces, such as electrostatic or hydrophobic forces and are very sensitive to environment (ionic strength, pH) [24]. From the pharmaceutical point of view, drug–protein adsorption is decisive in pharmacokinetics by controlling the free fraction of drug that can be dedicated to therapeutic effect. Large protein binding can decrease the free drug concentration, while weak binding may result in quick systemic elimination [25]. Hence, insight into the mechanism of drug–protein adsorption, along with modelling methodologies is important to enhance design of formulation attributes, dosing schedule, and therapeutic efficacy.

### 5.2 Protein Corona Formation on Drug Carriers

In the context of nanocarrier-based drug delivery systems, adsorption processes are known to give rise to what it is called a protein corona, which refers to biomolecule layer acquisition upon contact with biological fluids [26]. The structure and composition of protein corona are mainly affected by the physicochemical properties of carrier surfaces such as surface charge, hydrophilicity and roughness. The successful formation of protein corona modifies the effective surface properties of drug carriers and thereby affects cellular internalization, biodistribution and clearance pathways [27]. From the physicochemical point of view, corona formation is a competitive adsorption process in which proteins with larger surface affinity gradually displace those that are bound weaklier. This dynamic equilibrium emphasizes that the surface chemistry of drug nanocarriers should be modulated for rational pharmaceutical design [28].

### 5.3 Adsorption at Cell Membrane Interfaces

Cell membranes are complicated biological adsorption surface, which has inhomogeneous component and anisotropic feature. Drug adsorption onto membrane interface Drug adsorption at membrane interfaces is predominantly driven by electrostatic interactions with phospholipid headgroups and hydrophobic interactions within lipid bilayers [29]. Rigorous physicochemical regulation of membrane adsorption is thus a necessary requirement for the modulation of the drug permeation and transport across living barriers. Surface functionalized carriers that show increased adsorption affinity for particular membrane components can also assist in promoting cellular uptake while allowing maintenance of membrane integrity [30]. Such aspects have importance on the rational design of adsorption-mediated drug delivery systems as depicted in Figure 4.

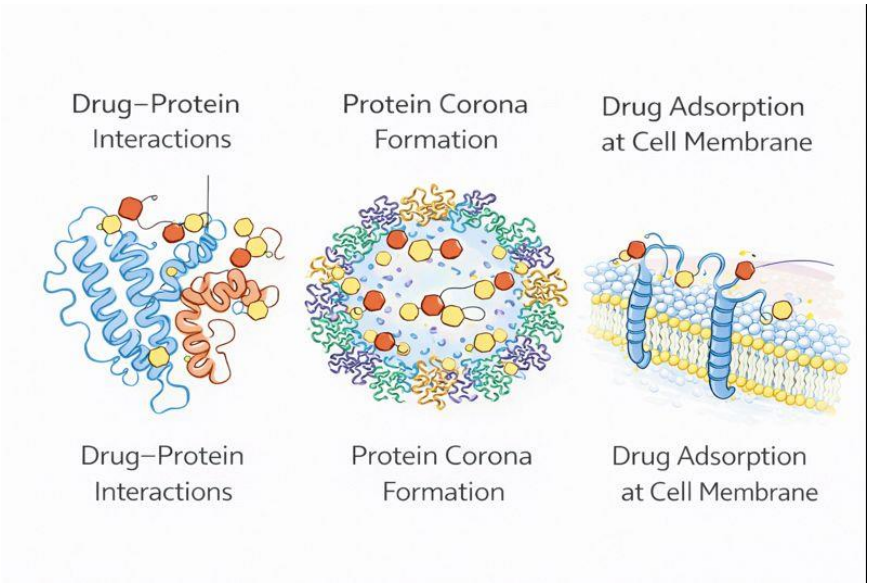


**Figure 4: Conceptual illustration of physicochemical adsorption at biological interfaces, including drug–protein interactions, protein corona formation, and drug adsorption at cell membranes (authors' illustration).**

## 6. Adsorption in Pharmaceutical Formulation Design

The adsorption is intentionally used in the pharmaceutical formulation design, as to control drug distribution, destabilization and release profile. From a physicochemical viewpoint, the formulation excipients, binders and carrier materials represent adsorption substrates which control drug−surface-interactions and thereby impact on the performance of formulations [31].

### 6.1 Drug–Excipient Adsorption

Drug molecule adsorption on the excipient surfaces is a critical phenomenon during the formulation of solid oral dosage forms. Excipients like silica, microcrystalline cellulose, and polymeric binders present a large specific surface area for uniform drug distribution and formulation stabilization [32]. Hence in formulation development, drug-excipient surfaces can be considered as being physiochemically compatible. Nevertheless, excessive adsorption could decrease drug availability by sequestrating the molecules onto excipient surfaces. Therefore, the desirable dissolution behavior and controlled release profiles can only be obtained through a careful balancing of adsorption affinity via surface alteration with formulation optimization [33].

### 6.2 Adsorption and Solid-State Stability

Adsorption plays a critical role in the solid-state properties of pharmaceuticals through its effects on crystallinity and polymorph stabilization. The adsorption of drug molecules onto the high–surface-area carriers can stabilize the amorphous state, which in turn enhances dissolution rate and thus bioavailability [34]. This stabilization is due to a limitation of molecular mobility on adsorbent surface from the point of view of physicochemical. Manipulation of the principles controlling stabilization upon adsorption allows for a systematic design of solid formulations with enhanced performance and prolonged storage stability [35].

### 6.3 Adsorption-Controlled Release from Solid Dosage Forms

Adsorption is an important mechanism in controlled-releasing preparations controlling drug release kinetics. Drug molecules adsorbed on carrier surfaces are desorbed and released by the combined effects of desorption and diffusion, which can be controlled via surface chemistry, porosity or morphology of carriers [36]. Such models that describe adsorption-mediated release, furnish quantitative methods for predicting the behavior of formulations and optimizing therapeutic efficiency [37]. These models mostly take into account physicochemical parameters such as adsorption affinity and diffusion coefficients to predict the release behavior of a drug, shown in Figure 5.

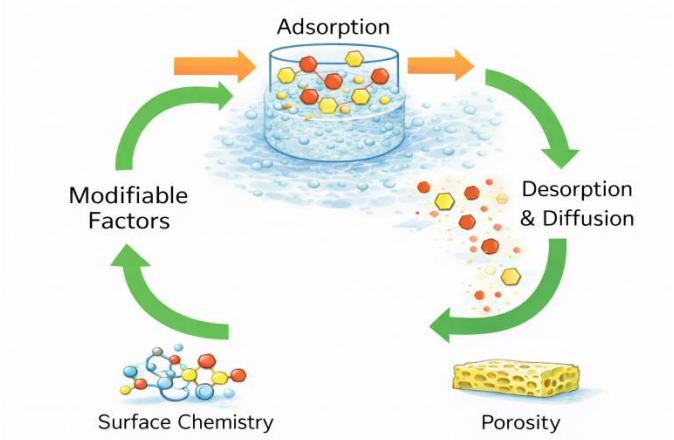


**Figure 5: Conceptual illustration of drug–excipient interactions and adsorption-controlled drug release in solid dosage forms, highlighting the role of adsorption in pharmaceutical formulation design (authors' illustration).**

## 7. Adsorption-Based Drug Delivery Systems

Adsorption based drug delivery systems are becoming effective means of controlling the load, release and targeting of drugs through physicochemical interactions on their surface. From the point of view of physical chemistry, such systems depend on a delicate balance between adsorption affinity and desorption kinetics to control drug delivery to the action site [38].

### 7.1 Adsorption on Porous and Nanostructured Carriers

Porous carriers (e.g., mesoporous silica, activated carbon, or polymeric matrices) offer high surface areas that significantly improve the drug absorption capacity [39]. The physicochemical characteristics of these carriers like pore-size distribution, surface functional groups, and surface energy play an important role in the adsorption behaviour and drug loading efficiency [40]. In mesoporous silica, drug molecule adsorption into specifically ordered pores is driven by electrostatic and hydrogen bonds as well. Localization of the drug molecule within nanometer-sized pores limits molecular mobility and thereby achieves long-term controlled release rates [41].

Adsorption in several of these systems can be described well by Langmuir-type isotherms, suggesting monolayer adsorption along the walls of the pores [42].

### 7.2 Adsorption-Controlled Release Mechanisms

In adsorption-controlled delivery systems, the release of drugs is regulated by the desorption-diffusion interface. Physiochemically, the rate of discharge is governed by affinity between drug & surface and availability of adsorption sites [43]. The stronger adsorption interactions tend to offer sustained drug release, while the weaker ones can result in faster drug discharge. Theoretical models coupling adsorption with diffusion are widely used to predict the drug release from porous carriers [44]. These models are quantitative tools to optimize the formulation parameters and to obtain targeted drug release profile.

### 7.3 Surface-Modified Carriers and Targeted Delivery

Surface Functionalization of Drug Carriers An effective strategy for tailoring adsorption interactions is surface modification of drug carriers. Surface modification of these NPs with charged, hydrophilic or bioactive groups changes the surface affinity to drug molecules and biological interface which allows selective absorption and targeted delivery [45, 46]. The differential accumulation of drug at specific vs. nonspecific sites through these adsorption-based targeting strategies emphasizes the significance of adsorption principles in designing intelligent advanced DDS [47].

### 8. Therapeutic and Environmental Implications

Adsorption has therapeutic and environmental implications that transcend those of formulation and delivery. In drug therapy, controlled adsorption dominates drug bioavailability, release pattern and safety, which may facilitate prolonged therapeutic effectiveness and enhanced patient compliance [48]. From an environmental perspective, adsorption will affect the fate, transport and persistence of pharmaceuticals in soil and aquatic ecosystems. Therefore, adsorption-based and nanotechnology-assisted delivery systems would provide an approach to improve therapeutic effectiveness as well as environmental burden in terms of controlled release of the drugs and reduced dosage [49, 50].

### 9. Challenges and Future Directions

Although many achievements have been made to develop adsorption-based pharmaceutical delivery systems, it is increasingly challenging to handle surface heterogeneity, biological complexity and competitive adsorption in the actual application environment. The gulf between lab-scale experiments and biological settings must be closed through combined experiments and state-of-the-art physicochemical models. New emerging trends are related to multiscale modelling and smart carrier systems able to modulate, in an on-off mode, the adsorption process according to environmental or biological stimulus [51, 52].

## 10. CONCLUSION

Adsorption, as an important physicochemical phenomenon, plays a crucial role in the drug behavior on material and biological interfaces. Surface properties, adsorption affinity, and the competition between thermodynamic and kinematic factors essentially determine the drug loading/release kinetics and interfacial interaction. In the light of complexity of pharmaceutical systems, selection of proper adsorption models is critical and should consider surface heterogeneity, carrier architecture, as well as drug physicochemical characteristics. One an uncontrolled adsorption can damage bioavailability and therapeutic efficacy, while controlled the other sustained release of the formulation. In total, combined adsorption will gradually provide a rational approach for designing new and advanced drug delivery systems.

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