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Kinetic and Thermodynamic Studies for Ciprofloxacin Hydrochloride Adsorption from Aqueous Solution on CuO Nanoparticles

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Abstract : Adsorption is the most versatile and widely used method for the removal of pollutants due to its high efficiency and ease of operation at large scale. In recent years nano metal oxides have been extensively used for the removal of pharmaceutical pollutants from waste water. In the present study, the adsorption behaviour of ciprofloxacin hydrochloride from aqueous medium, using CuO nanoparticles (synthesized by precipitation method)has been studied using batch experiments. The nanoparticles are characterized using X-Ray Diffraction, U.V and TEM. The average particle size, as determined from the XRD data, is 19.96 nm.The effects of initial drug concentration in the range 10-100mg/l, contact time 15-165 mins.pH entire range and the effect of temperature in the range 25^0–45^0Con the adsorption capacity have been studied.

Maximum removal 81.5% has been observed at pH 4 for a contact time of 135 min and drug concentration 100 mg/l, with an adsorbent dose of 100mg/10ml at temperature 298 K. Data obtained at optimum conditions have been subjected to isothermmodeling viz Freundlich, Langmuir, Temkin and Dubinin-Radushkevitch. The experimental data fits well to all the isotherm models with high correlation coefficient values.The experimental data fits to the first order rate equation and process follows first order kinetics. A study of intraparticle diffusion using the Morris Weber model shows that intraparticle diffusion occurs but is not the rate determining step. Thermodynamic parameters suggest the process to be exothermic and spontaneous with increased randomness at the solid solution interface.

Keywords: Adsorption, Batch studies, Isotherm analyses, Kinetics, Thermodynamic parameters.

1. Introduction:

Increase in health risks due to indiscriminate disposal of drugs in aqueous environment and pharmaceutical contamination in ground water system has been a cause of great concern due to harmful effects on environment[1]. A large number of pharmaceutical industries are releasing toxic contaminants in the environment directly or after chemical modification[2]. On the other hand, waste from hospitals, house hold waste and human excretion also contribute drug contamination[1].Fluoroquinoloneshave been generally detected in aqueous environment in the concentration range 1-100 µg/L[3,4].Ciprofloxacin hydrochloride {(1-cyclopropyl-6-fluoro-1,4-dihydro-4-oxo-7-(1-piperazinyl)-3-quinoline carboxylic acid)} isa commonly used broad-spectrum antibiotic agent of fluoroquinolone family[3,4]. The detected amount of these antibiotics in waste water is very minute but they are highly toxic for human, animal and aquatic lives even at very low concentration[5] and cause health problems like headache, diarrhea, tremors, nausea, vomiting, etc[5]. Several techniques such as

photocatalysis[6], advanced oxidation processes[7,8]and adsorption using different adsorbents e.g. activated carbon[9], sawdust[4], agricultural waste, and titanium oxide[10]has been reported for removal of fluoroquinolones. However, among these methods, adsorption has some advantages due to its high selectivity, high removal efficiency, ease of operation and lower cost[7]. Recently, nano metal oxides have become efficient and cost effective adsorbents for the removal of these pollutants. As compared to other adsorbents nano sized particles have high effectiveness to adsorb pollutants from water because of small size and large surface area[10,11].However, a single reference was found related to the use of Copper oxide nanoparticles for removal of metronidazole using photocatalytic degradation[6].Various literature reports have been found related to synthesis of CuO nanoparticles[12,13].Precipitation method[12]has been used for the preparation in the present study.The objectives of the present study are to evaluate theefficiency of CuO nanoparticles as adsorbent for the removal of ciprofloxacin hydrochloride from water in order to obtain an optimum set of conditions such as initial drug concentration, pH, contact time and temperature for maximum removal.

2. Materials and Methods

2.1. Preparation of CuO Nanoparticles

CuO nanoparticles have been synthesized using reported mehod[16] by mixing 300ml of 0.02 M copper acetate aqueous solution with 1 ml glacial acetic acid in round- bottomed flask equipped with a refluxing device. The solution was heated to 100 ^{o}C with vigorous stirring and approximately 0.8 gm. of NaOH pellets were rapidly added to the above boiling solution until pH value of the mixture was between 6-7, a large amount of black precipitate were formed simultaneously. After being cooled to room temperature, precipitates were centrifuged, washed with distilled water and dried in air at room temperature. The sample of CuO was characterized by X-ray Diffraction (Powder Method), Panalytical.sX.Pert Pro, UV (UV-Visible 2450 spectrophotometer, Shimadzu, Japan)and TEM, Hitachi(7500)[13,14].

2.2. Preparation of Adsorbate Solution

Opthalmic ciprofloxacin hydrochloride ($C_{17}H_{18}FN_3O_3{\cdot}HCl{\cdot}H_2O$, mol. wt. 385.82) with purity 99.8% (contain 3000 mg/l of drug) (Cipla) was used[19]. A stock solution of ciprofloxacin hydrochloride having drug concentration 100 mg/l was prepared in double distilled water. Further dilutions were carried out with double distilled water to obtain the concentration desired for the study (ranging from 10 mg/L to 100 mg/L).

2.3. Estimation of ciprofloxacin

Drug solution of concentration 100 mg/l was diluted to prepare the working standard solutions of concentration range 1 mg/l to 10 mg/l.U.V- visible spectrophotometer,(Shimadzu 2450, Japan) with 1 cm optical path length quartz cells was used for all absorbance measurements[15].Calibration curves were plotted for the estimation of drug for the pH range of 1-14 with different λ_{max}. Linear calibration plot of ciprofloxacin hydrochloride for the concentration range 1mg/l to 10mg/l at pH-4 gives λ_{max} at 275 nm. Water used as blank[19].

2.4. Batch Adsorption Studies

A known weight of adsorbent (100 mg) was placed in contact with 10 ml of ciprofloxacin hydrochloride solutions in the concentration range (10 mg/l to 100 mg/l) for time intervals varying from 15 mins. to 165mins. (till attainment of equilibrium) at varying pH (1-14), adjusted by the addition of 0.1M HCl / NaOH as the case may be. The samples were subjected to agitation and the resultant solutions were centrifuged and supernatant liquids analysed for drug content. To calculate the thermodynamical parameters for adsorption experiments were performed at varying temperatures ranging from 25^{o} to 45^{o} C at pH 4 ,drug concentration 100mg/land contact time 135 minutes.

3. Results and Discussion

3.1. Characterization of CuO Nanoparticles

3.1.1 XRD studies

The XRD pattern of CuO nanoparticles obtained showed peaks at scattering angle(2θ) of 32.5265, 35.5022, 38.6928, 53.5068, 58.1202, 61.0685, 68.0489 corresponding to the reflection from (111), (111), (202), (020), (202), (113), (311) planes respectively (Fig.1(a)). It indicates a single-phase CuO with a monoclinic structure. This XRD pattern also points towards the purity of CuO nanoparticles. The peaks are broad due to nano-size effect. Similar results have been obtained by Lanje[13] for the study of synthesis and optical characterization of copper oxide nanoparticles. The average diameter of synthesized CuO nanoparticle was calculated using Debye-Scherrer formula[14]was found to be 19.96nm.

$$D = 0.89\ {}^{\lambda}/_{b} \cos\theta \qquad (1)$$

Where 0.89 is the Scherrer's constant, λ is the plane located at 36.24°.

3.1.2 UV-Spectral studies

The UV absorption spectrum exhibits a strong absorption band at about 278 nm, indicating that CuO nanoparticles did not flocculate and sink from the suspension and the suspension is stable, which also shows that the obtained CuO are well-dispersed particles[13].

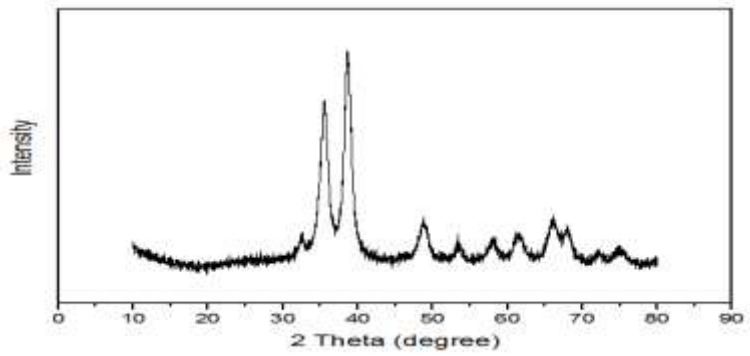

Fig. 1(a):XRD pattern of prepared CuO nanoparticles

3.1.3 TEM study

In order to evaluate the particle size of CuO nanoparticles, transmission electron microscopy was performed. Fig. 1(b) shows the transmission electron microscopy (TEM) image of CuO nanoparticles. This image shows that the size of CuO nanoparticles is very consistent. The average particle size was estimated to be 20 nm[6].

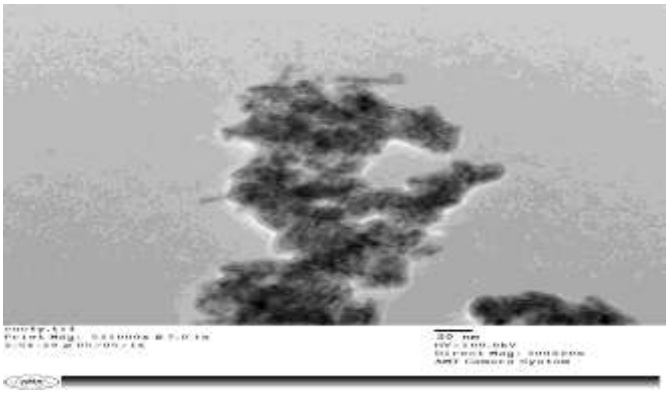

Fig. 1(b):TEM images of CuO nanoparticles

3.2. Effect of Initial Concentration and Contact Time

As is apparent from Figure 2, amount of drug adsorbed increases with concentration in the concentration range studied, however, percentage removal decreases with increase in drug concentration. The increase in percentage adsorption with dilution is due to the availability of larger number of adsorbent sites for a smaller number of drug species for adsorption[23]. Maximum removal takes place in the initial 15 minutes and after that increases very slowly (Fig. 2) until equilibrium is attained at 135 min. This may be explained on the basis that number of available adsorption sites decreases with time[4,17].Maximum adsorption occurs for a solution of concentration 100mg/L for a contact time of 135 mins.

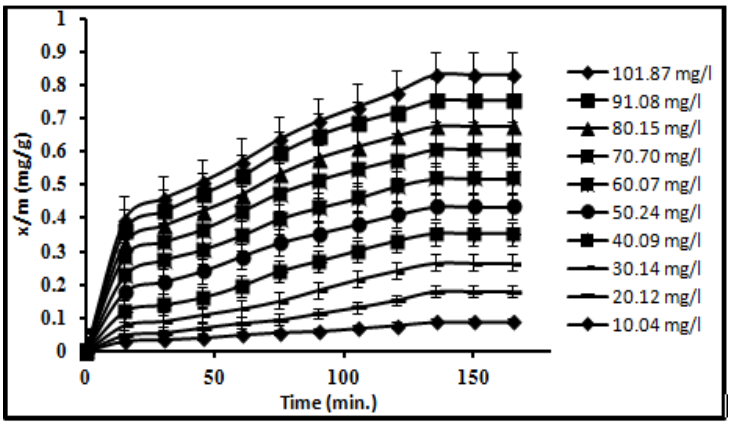

Fig. 2:Amount of ciprofloxacin hydrochloride adsorbed (mg g^{-1}) *vs*time (min.) at different drug concentrations at pH-4

3.3. Effect of pH

The pH of the adsorbate solution was varied from1 to 14 for a contact time of 135 min. and drug concentration 100mg/l. The removal increases with increase in pH from 1 to 4 (Fig. 3), thereafter increasing the pH leads to a decrease in amount adsorbed, this can be explained on the basis that at low pH value the H^+ ions present in solution compete with cationic group of the ciprofloxacin hydrochloride[4].However at pH 4 the adsorption of ciprofloxacin is maximum. As pHis increased beyond 7, the OH^- ion concentration is increased and adsorption decreases probably due to the competition of the drug molecules with excess hydroxide ions (OH^-) for the adsorption sites resulting in lower adsorption[3,4].

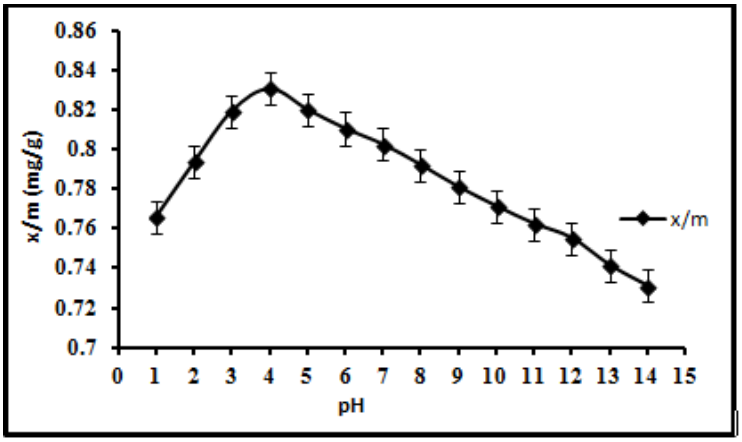

Fig. 3:Effect of pH on amount of ciprofloxacin hydrochloride adsorbed for a contact time of 135 minutes and drug concentration 100 mg/l

3.4. Adsorption Isotherm Modelling

The data for the removal of ciprofloxacin hydrochloride by CuO nanoparticles at pH-4 and contact time of 135 minutes have been analyzed using various isotherm models

3.4.1. Freundlich isotherm

The linearised form of the Freundlich equation can be given as[4]:

$$log\, q_e = log\, K_f + {}^{1}/_{n}\, log\, C_e \qquad (2)$$

Where C_e is the equilibrium concentration (mgL^{-1}) and q_e is the amount adsorbed (mgg^{-1}). The data fits to the Freundlich isotherm model and the values of n and K, determined from slope and intercept of the linear plot of log q_e vs. log C_e are 1.27 and $0.930 mgg^{-1}$ respectively. The value of $1<n<10$ suggest the effectiveness of the adsorbent[4,18]. This suggests applicability of Freundlich isotherm with high R^2 value of 0.9845 suggesting favourable and monolayer adsorption.

3.4.2. Langmuir adsorption isotherm

Langmuir equation[24] is given by Eq.3:

$${C_e}/{q_e} = {}^{1}/_{K_L} + {}^{a_L}/_{K_L}\, C_e \qquad (3)$$

whereC_e is the solute phase concentration(mg/L), q_e is the amount of solute adsorbed per unit weight of adsorbent(mg/g), K_L related to affinity of the binding sites(Lmg^{-1}), a_L the Langmuir isotherm constant can be determined from a plot of C_e/q_e against C_e. Values of constants a_L and K_L are 0.051 and 0.886 L/mg for CuO nanoparticles from straight line plot ofC_e/q_evsC_e indicates that the adsorption of ciprofloxacin on both the adsorbents obeys Langmuir isotherm[4,18] High R^2 value shows that the experimental adsorption datafits well to the Langmuir isotherm model.

In order to know the feasibility of the isotherm, the essential features of Langmuir model can be expressed in terms of separation factor or equilibrium parameter R_L,

$$R_L = {}^{1}/_{(1 + a_L C_e)} \qquad (4)$$

The value of R_L lies between 0 and 1 for a favorable adsorption, while $R_L > 1$ represents an unfavorable adsorption, and $R_L = 1$ represents the linear adsorption, while the adsorption operation is irreversible if $R_L = 0$.The values of R_L are found to be 0.51indicating that favorable adsorption occurs[17].

3.4.3. Temkin isotherm

Temkin isotherm is based on the fact that the heat of adsorption of all molecules decreases linearly with the coverage of molecules due to the repulsion in adsorbate-adsorbate molecules and the adsorption of adsorbate is uniformly distributed[3]. The Temkin equation is given as

$$q_e = B_T\, ln\, A_T + B_T\, ln\, C_e \qquad (5)$$

Where, q_e is the amount of solute adsorbed per unit weight of adsorbent(mg/g), $B_T = (RT)/b_T$, is constant related to heat of adsorption ($Jmol^{-1}$), T is absolute temperature (K) and R is universal gas constant, 8.314 J mol^{-1} K^{-1}. The constant $b_T$is Temkin isotherm constant and has been found to be 8.95×10^2, A_T is the equilibrium binding constant (lg^{-1}) corresponding to maximum binding energy[4]. The values of the isotherm constants A_T and B_T have been found to be 0.886 lg^{-1} and 2.766 J/mol respectively as obtained from the slope and intercept of the plot of q_e vs. lnC_e which is a straight line (Fig. 4) indicating that applicability of Temkin isotherm.

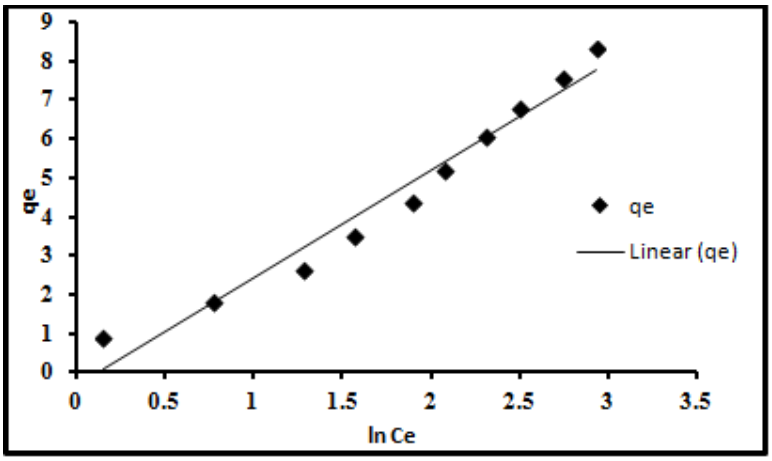

Figure 4 Temkin Isotherm for adsorption of ciprofloxacin at pH–4 for CuO nanoparticles at 298 K for contact time 135 min.

3.4.4. Dubinin-Radushkevitch (D-R) isotherm

Dubinin-Radushkevitch isotherm is represented by[4]:

$$ln\, q_e = ln\, Q_m - K\, \varepsilon^2 \quad (6)$$

where K (mol^2 kJ^{-2}) is a constant which relates to adsorption energy, Q_m(mg g^{-1}) is the maximum adsorption capacity, The polanyi potential Ɛ, can be expressed as

$$\mathcal{E} = RT\, ln\, (1 + 1/C_e) \quad (7)$$

Where R is universal gas constant, 8.314 J mol^{-1}K^{-1}, T is absolute temperature (K) and C_e is the drug equilibrium concentration (mgL^{-1}). The D-R isotherm constants, K and Q_m can be calculated from the plot of lnq_e and Ɛ^2. The values of K and $Q_m$are found to be 0.238 mol^2 kJ^{-2} and 10.6 mg g^{-1} respectively. Using the value of K, it was possible to evaluate the mean sorption energy E (kJ mol^{-1}) from Eq.8

$$E = K^{-1/2} \quad (8)$$

The value of E is found to be 2.04 lies b/w 1-16 kJ mol^{-1} indicates that physical adsorption is taking place[3,4].

3.5. Kinetic Studies

The adsorption data obtained at pH 4 for ciprofloxacin concentration 100 mg/l and contact time of 135mins. has been taken for a study of the kinetics of adsorption of ciprofloxacin on copper oxide nanoparticles. Using the basic rate equation[17]

$$r = k\, C^n \quad (9)$$

Where R is the adsorption rate (mgg^{-1}min^{-1}), k is rate constant (min^{-1}), C is concentration (mg/L) and n is the order of reaction. A straight line plot for log R vs. log C gives the values of rate constant k and order of reaction nto be 0.0069 min^{-1} and 0.7926 respectively. The value of n indicates that the adsorption follows first order kinetics.

The results are further substantiated by using the Lagergren first order equation:

$$log\, (q_e - q) = log\, q_e - k_{ad}\, X\, t/\, 2.303 \quad (10)$$

whereq_e and q (mg g^{-1}) are the amounts of drug adsorbed at equilibrium and at any time taken for study respectively, t (min) is the time of contact and k_{ad} is the adsorption rate constant (min^{-1}). The rate constant k_{ad} (min^{-1}) has been found to be 0.019and value of amount adsorbed at equilibrium q_e (mgg^{-1}) is 6.88from plot of log(q_e − q) vs. t which is a straight line indicating the first-order kinetics[3].

Intra-Particle Diffusion Study

The possibility of intra-particle diffusion has been studied by Morris Weber model (Eq. 11), by plotting the amount adsorbed per unit weight of adsorbent (q) vs. $t^{1/2}$

$$q = K_p \; x \; t^{1/2} \qquad (11)$$

where q is the amount of drug adsorbed in mg for 1g of adsorbent at different time intervals (mgg^{-1}), K_p is the intraparticle diffusion constant (mgg^{-1} min^{-1})and t is contact time (min.). K_p as calculated from the slope of the linear plot of q vs $t^{1/2}$and has been found to be 4.4404 $mgg^{-1}min^{-1}$. A straight line plot has been obtained, but does not pass through origin, that shows intraparticle diffusion occurs but is not the rate determining step[3,17].

3.6. Effect of temperature

The effect of temperature was investigated by varying temperatures ranging from 25° - 45° C. The amount of drug adsorbed increases from 0.830 to 0.844 to 0.857 mg/g with increase in temperaturefrom 298 K to 308K and 318K respectively. The increased sorption with increase in temperature is also due to increase in number of sorption sites generated because of breaking of some internal bonds near the active surface sites of adsorbent[5].

3.7. Thermodynamic Studies

Thermodynamic parameter such as change in the free energy ΔG^0KJ/mol), enthalpy (ΔH^0) (KJ/mol) and entropy (ΔS^0) (J/K/mol) were determined using the following equation:

$$K_o = {}^{C_{solid}}\!/_{C_{liquid}} \qquad (12)$$

$$\Delta G^o = -RT \ln K_o \qquad (13)$$

$$\log K_o = {}^{\Delta S^o}\!/_{(2.303R)} - {}^{\Delta H^o}\!/_{(2.303RT)} \qquad \square\square\square\square$$

Where K_0 is the equililibrium constant,C_{soild} is the solid phase concentration of equilibrium (mg/l),C_{liquid} is the liquid phase concentration at equilibrium (mg/l), T is the temperature in degree Kelvin and R is gas constant[3]. Van't Hoff plot of lnK_oVs 1/T gives the values of enthalpy (ΔH^0 **)** and entropy (ΔS^o **)**change from the slope and intercept respectively (Fig. 5). The value of ΔG^0 is found to be (-4.137 x 10^3) and negative values of ΔG^0 indicate feasibility and spontaneous nature of adsorption. The values of ΔH^0 and ΔS^0 are 7.898 x 10^3 and 35.35 respectively. The positive value of ΔH^0 suggests the endothermic nature of adsorption. The positive value of ΔS^0 suggests the increase in randomness at solid solution interface during adsorption[3].

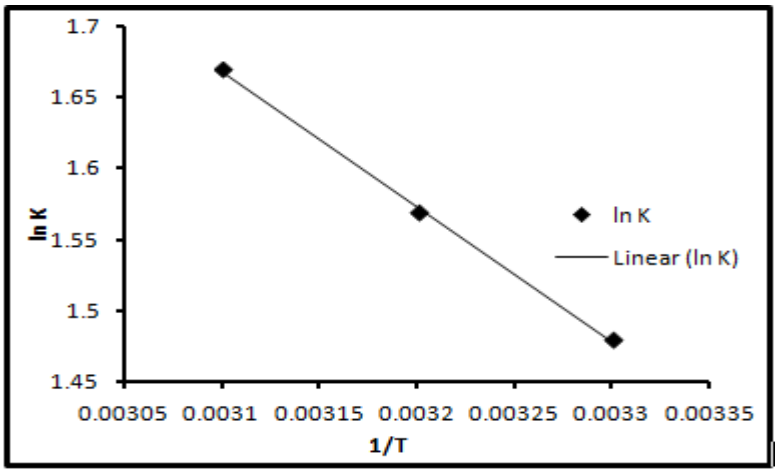

Fig.5:Van't Hoff plots for adsorption of ciprofloxacin on CuOnanoprticles at initial drug concentration 100mg/l at pH-4

4. Conclusions

Studies suggest that CuO nanoparticles can be used as an effective adsorbent for the removal of ciprofloxacin hydrochloride from aqueous solution. Adsorption isotherm studies suggest physical andmonolayer adsorption. Kinetic studies reveal that the process follows first order kinetics,and thatintra-particle diffusion occurs but is not the rate determining step.The value of thermodynamic parameters indicatefeasible and spontaneous nature of adsorption which is endothermic and proceeds with increase in randomness at the solid solution interface.

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