

Comment

# Analytical Continuation within the Freundlich Adsorption Model. Comment on Edet, U.A.; Ifelebuegu, A.O. Kinetics, Isotherms, and Thermodynamic Modeling of the Adsorption of Phosphates from Model Wastewater Using Recycled Brick Waste. *Processes* 2020, 8, 665

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**Abstract:** Using experimental data for the adsorption of phosphates out of wastewater on waste recycled bricks, published independently in *MDPI Processes* before (2020), this message re-visits the mathematical theory of the Freundlich adsorption model. It demonstrates how experimental data are to be deeper treated to model the saturation regime and to bridge a chasm between those areas where the data fit the Freundlich power function and where a saturation of surface adsorption centers occurs.

**Keywords:** freundlich isotherm; adsorption; saturation

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The usefulness of the Freundlich adsorption function

$$q/q_{\infty} = Kx^{\alpha} \quad (1)$$

where  $x$ ,  $q$ , and  $q_{\infty}$  stand for pressure (ionic activity or bulk concentration for solutions with a constant ionic power), current adsorption, and limiting adsorption, respectively, the power of  $x$  is often considered as  $\alpha = 1/n$ , where  $n > 0$  is an integer or real number, in both historical and modern research can scarcely be overestimated. This is monograph [1], which first convincingly elucidated the meaning of Equation (1) for interpretation of experimental data. Nowadays, the Freundlich isotherm finds itself among a de facto standard set of those (also the Langmuir, Temkin, and Dubinin–Radushkevich isotherms) through which experimental data are to be nearly inevitably checked. An open list of phenomena and processes, the Freundlich adsorption model is inherent in, involves hundreds or even thousands of heterogeneous systems. To avoid making unsubstantiated statements, we refer to some of them, the first of which published in *MDPI Processes* in 2020 and considered in this message in more detail is the adsorption of phosphates out of wastewater on recycled brick waste [2] as well as the others on the adsorption of lead(II) on activated carbon [3] and improvement in bioactivity with protein through the use of its carrier nano-Mg(OH)<sub>2</sub> [4]. In these and many other works, “well established methodologies (e.g., fitting adsorption data to a Langmuir or Freundlich isotherm)” [5] have been used, and further analysis is being performed with respect to the pressure or concentration range the experimental data were obtained within. The purpose of this message is to remind the community that even limited experimental data enable one to perform a more extensive analysis.

For these purposes, we re-visit Zeldowitch’s theory of the Freundlich isotherm, developed in 1934 [6], and later re-produced as one of the parametrical limits while expanding

the general solution for energetically heterogeneous surfaces through a hypergeometric function into an infinite series in [7,8]. In the sense of a surface energetic heterogeneity, the Freundlich adsorption model proper for exponentially heterogeneous surfaces occupies the rightmost place in the sequence Langmuir (homogeneous surfaces)—Temkin (evenly heterogeneous)—polylogarithmic model (linearly heterogeneous)—a power law heterogeneity—Freundlich [9].

The limiting adsorption is bounded through the surface available and an effective number of layers (should it be multi-layer). As follows from the functional form itself of Equation (1), it does not describe a saturation regime, so that deviations from Equation (1) appear at big  $x$ . It has become typical for the experimental (and not only) research community that data obtained and analyzed in the framework of the Freundlich adsorption model are typically checked for their relevance to Equation (1) with a successive determination of constants  $K$  and  $\alpha$  as a must ([2–4] serve as examples). Nevertheless, Zeldowitch's theory for the Freundlich adsorption model goes beyond the small and moderate coverages and also mathematically describes the saturation regime. Furthermore, it appears possible to link the area of small coverages and that at saturation. Furthermore, Zeldowitch's theory is applicable to both mono- or multi-layer adsorption. In the last case, one has to distinguish between successive adsorption of layers "one after one" like a staircase and simultaneous adsorption when successive layers are being filled without completely filling the foregoing ones. For the former, the theory is to be applied to each of the "stairs" separately.

Zeldowitch considered the problem of finding such a distribution  $a(b)$  of surface adsorption centers on their adsorption heat where the local application of the Langmuir adsorption model would lead to an overall functional form (1) for the whole surface. Mathematically, this meant solving the integral equation:

$$q(x)/q_{\infty} = \int_0^{b_0} \frac{a(b)x}{x+b} db \quad (2)$$

where the upper limit  $b_0$  was introduced artificially to enforce the integral convergence. Since Equation (2) was found to be intractable with respect to  $a(b)$ , the problem was simplified through the following replacement: instead of the Langmuir isotherm in Equation (2), the following local adsorption function was substituted into Equation (2):

$$\begin{cases} \frac{ax}{b}, & \text{if } x \in (0; b] \\ a, & \text{if } x \in (b; b_0] \end{cases}$$

With such a kernel function in Equation (2), distribution function  $a(b) = Ab^{\alpha-1}$  was obtained and shown to meet Equation (2), should the isotherm have the form as Equation (1). The following relationships appear to be an integral part of Zeldowitch's theory: at small  $x$

$$\lim_{x \rightarrow 0} \frac{q(x)}{q_{\infty}} = \left(\frac{x}{b_0}\right)^{\alpha} \frac{\pi/n}{\sin \pi/n} \quad (3)$$

whereas for big  $x \gg b_0$ , one has

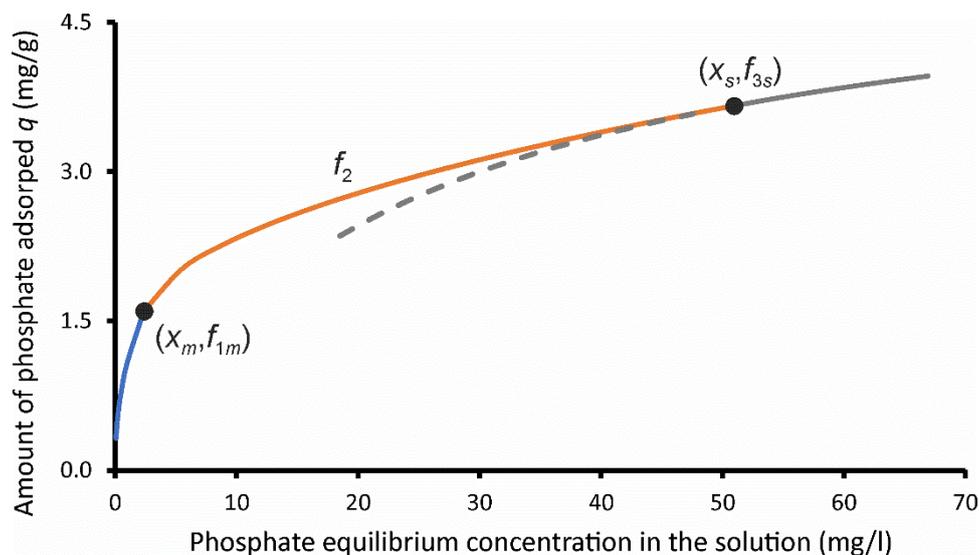
$$\frac{q(x)}{q_{\infty}} = 1 - \frac{b_0}{\left(1 + \frac{1}{\alpha}\right)x} + \dots \approx \frac{x}{x + b_0 \left(1 + \frac{1}{\alpha}\right)} \quad (4)$$

Thus, should constant  $b_0$  be approximately determined on the basis of experimental data according to Equation (3) as

$$b_0 = \lim_{x \rightarrow 0} x \left( \frac{q_{\infty}}{q(x)} \frac{\pi/n}{\sin \pi/n} \right)^{1/\alpha}, \quad (5)$$

the saturation regime (4) at big  $x$  also appears to be identified.

According to the above stated, dependencies like Equation (1) appear to be determined and carefully studied on the basis of small and/or moderate pressures that includes the determination of constants  $K$  and  $\alpha$  (blue curves in Figure 1). The saturation regimes (4) turn out to be, as a rule, omitted (shown grey in Figure 1) both in the experimental studies and discussions of obtained results. Nevertheless, there are many evident reasons why such regimes as well as intermediate regions (orange in Figure 1) can represent considerable interest for the research community.



**Figure 1.** Freundlich isotherm in all concentration ranges. Blue: experimental data [2], grey: saturation regimes according to Equation (4), orange: bridging the chasm for intermediate concentrations.

Technically, the most obvious way to model the intermediate region of concentrations would be to perform some interpolation. One needs to identify boundaries  $x_m$  and  $x_s$  of the intermediate area and to perform linkages on the class of continuously differentiable functions. Whereas boundary  $x_m$  is naturally given as the experimental data point for the maximum concentration (that belongs to an experimentalist's judgement whether the power law area has not been yet left there), point  $x_s$  is to be determined on the basis of some considerations depending on what point is corresponding to the beginning of a saturation regime. This would be a relative judgement. Furthermore, one has to check if the chasm between the low and high concentration regions admits bridging. The necessary conditions for this are

$$f_3(x_s) > f_1(x_m), \quad df_3(x_s)/dx < df_1(x_m)/dx \quad (6)$$

where the dependence due to Equation (1), determined in experiments is denoted as  $f_1$  and the dependence due to Equation (4) as  $f_3$ . If conditions (6) are not true, either approximation of the experimental data with Equation (1) went beyond the region in which the power law is indeed valid, or some other adsorption model than the Freundlich one was met in the experiment. The following linkage approach has been employed to make this message complete. To provide a smooth linkage, coincidence of the tangent lines within each pair  $(f_1, f_2)$  and  $(f_2, f_3)$  was considered at points  $x_m$  and  $x_s$ , respectively. For  $f_2$ , a quadratic form was employed. Out of the parabolic, hyperbolic, and elliptic forms was chosen parabola (the upper branch of  $f_2'^2 = 2px'$  in that Cartesian coordinate system with apostrophe where it has the canonical form) as that with the condition for the tangent line

$$f_2'f_2^{(0)'} = p(x' + x_0') \quad (7)$$

resulting in less cumbersome equations at a linkage point denoted here through sub-/superscript '0'. In order to facilitate linkage and at the same time provide a suf-

ficient number of linkage parameters, a translational transformation  $x' = x + c$ ,  $f'_2 = f_2 + d$  was applied to Equation (7). Thus, four parameters ( $c$ ,  $d$ ,  $p$  and  $x_s$ ) appeared to be determined through four equations at the linkage points at  $x_m$  and  $x_s$ . In other words, the right linkage point itself turned out to be determined within this procedure ( $x_s > x_m$  appears then the consequence of inequalities (6)). With a parabolic form, these four equations enable one to express  $c$ ,  $d$ , and  $p$  through  $x_s$ , leading to a single transcendental equation for  $x_s$  to be solved numerically. The following parameters were finally determined (Table 1).

**Table 1.** Linkage parameters for the system with adsorption of phosphates on recycled brick waste [2] (Figure 1).

Parameters	Magnitudes
experimental due to the source	
$K$	1.08
$\alpha$	0.4557
$x_m$	2.37
$f_{1m}(x_m)$	0.299
saturation asymptotical line for $f_3$	5.35
calculated	
$c$	−2.104
$d$	−0.268
$p$	0.00177
$b_0$ due to Equation (5)	75.195
saturation parameter $b = b_0 / \left(1 + \frac{1}{\alpha}\right)$ in Equation (4)	23.539
the infimum of $x_s$ according to Equation (6)	26.11
$x_s$	50.79
$f_{3s}(x_s)$	3.656

The most important practical result of the calculations performed seems to demonstrate how far from (or close to) the saturation regime the rightmost experimentally determined points find themselves. Besides this de facto addendum to the source work, one obtains the values of  $b = b_0 / \left(1 + \frac{1}{\alpha}\right)$  in Equation (4), which characterize the saturation tempo and, consequently, the adsorption properties of the surface with large coverage. The effectiveness of chasm bridging proposed in this message could be judged on the basis of experimental data to be obtained for the corresponding region. Even in the framework of the proposed approach, one could choose between at least three linkage options (i.e., parabolic, hyperbolic, and elliptical ones).

## Conclusions

Zeldowitch's theory of the Freundlich adsorption model was re-visited in the context of work [2]. The procedure of analytical continuation of the power law (i) to the saturation area was described and (ii) to the intermediate region was developed. This enables one to judge the saturation rate in the respective area and to bridge a chasm between low (moderate) and high pressure (activity or concentration). Experimental data for the adsorption of phosphates on recycled brick waste published in [2] were additionally treated to demonstrate how analytical continuation of the Freundlich isotherm works.

Zeldowitch underlined at the end of his work [6] that his goal was a contribution to the community's correct interpretation of experimental data rather than some quantitative theory of adsorption on heterogeneous surfaces. Similarly, we emphasize here that our goal

in having this message published was to contribute to the community's comprehensive analysis of experimental data having first been interpreted as complying with the Freundlich isotherm, but indeed as those to be essentially more comprehensively interpreted in the framework of the Freundlich–Zeldowitch adsorption model.

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