



Short communication

Deeper insights into fractal concepts applied to liquid-phase adsorption dynamics

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ABSTRACT

In this work, the superior accuracy of “fractal-like kinetic models” with respect to their classical counterparts in interpreting cadmium adsorption dynamics on both raw and beneficiated (by means of mechanical sieving and CO₂/steam gasification) combustion fly ashes has been validated. Results showed that classical and “fractal-like kinetic models” produce comparable outputs only for low fractional adsorption degrees (generally lower than 0.5); this was ascribed to a likely more homogeneous pollutant concentration in the particle outer shells. On the other hand, for longer adsorption times a less random pollutant intraparticle distribution should be responsible for a fractal-like behaviour. Additionally, for beneficiated ashes, the generally higher values of fractal pseudo-first order model rate coefficients (the model that produced best fitting results) with respect to what was observed for the parent sorbent, were linked to both the reduction of the particle diameter and the porosity development induced by the activation treatments, determining faster diffusion paths for the pollutant.

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1. Introduction

Adsorption is commonly recognized as an effective and versatile purification technology for the removal of numerous contaminants from liquid and gaseous effluents (such as organic compounds and heavy metals from wastewaters, and SO₂, NO_x, Hg and CO₂ from flue gas) due to the operating flexibility of the process, the potentially high selectivity towards a specific pollutant and the absence of by-products [1–10]. Industrial-scale adsorption processes are usually carried out either in cyclic batch systems, where an adsorbent fixed bed is alternately operated in adsorption and regeneration mode, or in continuous flow units with a countercurrent contact between the polluted stream and the adsorbent [6]. Contextually, the accurate description of the dynamic response of a fluid–solid adsorption unit requires adequate mathematical expressions for both adsorption equilibrium and kinetics, in order to establish the nature of pollutant–sorbent interactions and the capture mechanism. The prediction of the pollutant removal rate by adsorption is considered a more complicated problem than the theoretical analysis of the adsorption equilibrium, the latter characterizing only the final distribution of the contaminant between the solid and fluid phases independently of the complex time-dependent transport and capture steps involved in the process [11]. Many mathematical models have been developed to interpret kinetic adsorption data based on surface reaction (e.g. Langmuir and Langmuir–Freundlich models) or film–intraparticle diffusion mechanisms, or referring to the Statistical Rate

Theory and to compact formulas differing in the functional form adopted to express the dependence of the removal rate on the process driving force (such as pseudo-first and pseudo-second order or exponential kinetic model) [11–14]. Even if compact kinetic models have been applied to numerous adsorption systems due to their simplicity determining computational time-saving, it has been pointed out that they are able to provide an optimum data fitting only in specific time ranges [2,11,15]. All the aforementioned models assume time-invariant kinetic constants or transport properties. In this framework, Kopelman [16] was one of the pioneers in finding that classical reaction kinetics (constant kinetic parameters) is not applicable for heterogeneous diffusion-limited processes where the reactants are spatially constrained by walls, phase boundaries or force fields such as in porous solids. Observations, gathered from experiments and simulations performed for different processes occurring in geometric fractal-like media or onto surfaces exhibiting energetic heterogeneities, demonstrated time-dependent rate coefficients (fractal-like kinetics) [16,17]. Recently, Haerifar and Azizian [15,18] introduced new physical concepts to explain the fractal-like behaviour for adsorption processes: in the case of homogeneous surfaces, the fractal dependency of the rate coefficient was ascribed to the progressive occupation of the adsorption sites via slower pathways available for the adsorbate, whereas for heterogeneous sorbents the decrease of the kinetic parameter with time was related to the adsorption onto sites characterized by greater activation energies.

The literature scenario highlights that even if “fractal-like kinetic models” are very attractive for a more realistic description of fluid–solid adsorption dynamics, there is still big research challenging in establishing a link between the time dependence of rate coefficients and

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the adsorbent textural properties, which in turn could allow either a more accurate sizing of a dynamic adsorption unit and a more systematic selection of the sorbent microstructural features more apt to remove a specific pollutant from contaminated effluents. In this paper, the validation of the fractal approach for the description of cadmium adsorption onto fly ashes both raw and beneficiated (by means of mechanical sieving and CO₂/steam gasification) has been investigated. In particular, the results obtained from pseudo-first, pseudo-second order and exponential kinetic models in their classical and fractal-like forms were compared and analysed in the light of the sorbents granulometric and porosimetric properties. Experimental adsorption data and solid characterization results of reference for the modelling analysis and interpretation can be retrieved in recent papers published by this research group [2,19–21].

2. Materials and methods

2.1. Adsorbent materials and adsorption tests

A detailed description of the adsorbents chemico-physical and microstructural properties, together with the experimental protocols adopted for both sorbents activation and adsorption experiments can be found elsewhere [2,19–21]. More relevant information is here recalled for the sake of clarity.

The raw material employed for the adsorption experiments was a coal combustion fly ash (CCA), and starting from it three other sorbents were obtained by different beneficiation treatments: fly ash finer than 25 μm (sample F25) derived from mechanical sieving of the parent substrate, and fly ash gasified at 850 °C for 10 min with either CO₂ (dry gasification) and steam (samples DG10 and SG10, respectively).

Cadmium adsorption kinetic tests were carried out alternatively onto CCA, F25, DG10 and SG10 at room temperature and in batch mode by contacting 1 g of each sorbent with a 50 mg L⁻¹ Cd²⁺ aqueous solution (total volume 0.1 L) for times ranging from 10 min to 7 d. The analysis of the cadmium concentration in the liquid phase at each operating time (by means of atomic absorption spectrophotometry) allowed to follow the dynamic evolution of the sorbent specific adsorption capacity $q(t)$ (Eq. (1)) or the surface coverage degree with respect to equilibrium conditions, $\theta(t)$ (Eq. (2)) (see *Nomenclature*):

$$q(t) = \frac{(C_0 - C(t))V}{m} \quad (1)$$

$$\theta(t) = \frac{q(t)}{q_{eq}} \quad (2)$$

2.2. Kinetic data mathematical modelling

Modelling analysis of the dynamic patterns experimentally derived for cadmium adsorption onto the investigated sorbents was performed adopting the well-known pseudo-first order (PFO, Eq. (3)) and pseudo-second order (PSO, Eq. (4)) kinetic equations [11,18,22] together with the recently proposed exponential model (EXP, Eq. (5)) [12]:

$$\theta(t) = 1 - \exp(-k_{PFO}t) \quad (3)$$

$$\theta(t) = \frac{k_{PSO}q_{eq}t}{1 + k_{PSO}q_{eq}t} \quad (4)$$

$$\theta(t) = \ln \left[2.72 - 1.72 \exp \left(-\frac{k_{EXP}}{q_{eq}} t \right) \right] \quad (5)$$

The time invariance of the kinetic constants in classical models applies for systems in which convective or diffusive stirring determines

a randomly uniform distribution of the reactants, whereas in processes exhibiting a fractal-like behaviour segregation and self-ordering phenomena occur [16]. The following Eq. (6) was derived to express the rate coefficients exhibiting temporal “memories” [16]:

$$k_F = k' t^{-h} \quad 0 \leq h \leq 1 \quad (t \geq 1) \quad (6)$$

where h is a heterogeneity parameter [23,24]. In the limiting case $h = 0$, one recovers the classical kinetic formulation ($k_F = k'$, time-independent rate coefficient), valid for motion in locally homogeneous environments [24].

The assumption of a fractal dependence for the adsorption rate coefficient according to Eq. (6) allows obtaining the following integrated rate laws for the fractal-like pseudo-first order (FPFO, Eq. (7)), fractal-like pseudo-second order (FPSO, Eq. (8)) and fractal-like exponential (FEXP, Eq. (9)) models [18]:

$$\theta(t) = 1 - \exp \left(-\frac{k'_{FPFO}}{1-h} t^{(1-h)} \right) \quad (7)$$

$$\theta(t) = \frac{k'_{FPSO}q_{eq}t^{(1-h)}}{(1-h) + k'_{FPSO}q_{eq}t^{(1-h)}} \quad (8)$$

$$\theta(t) = \ln \left[2.72 - 1.72 \exp \left(-\frac{k'_{FEXP}}{q_{eq}(1-h)} t^{(1-h)} \right) \right] \quad (9)$$

Kinetic data modelling for cadmium adsorption onto CCA, F25, DG10 and SG10 sorbents was performed by means of non-linear regression of experimental $\theta(t)$ profiles according to pseudo-first, pseudo-second order and exponential models in their classical (Eqs. (3)–(5)) and fractal-like forms (Eqs. (7)–(9)). Best-fitting kinetic models were evaluated comparing both average relative error deviation (ARED) and hybrid fractional error function (HYBRID), which are considered to be more reliable statistical tools with respect to the determination coefficient (R^2) for non-linear modelling [25]. Finally, it is highlighted that only the kinetic constants (and the h exponents for fractal-like expressions) were let as fitting parameters for the adopted models, whereas q_{eq} values in the pseudo-second order and exponential models (canonical and fractal forms) were experimentally determined.

3. Results and discussion

3.1. Comparison between canonical and “fractal-like kinetic models”

Table 1 reports the main kinetic parameters derived from mathematical modelling of cadmium adsorption data onto the investigated adsorbents. As a preliminary consideration, it can be observed that, when the classical kinetic expressions are taken into account, the pseudo-second order model provides more accurate data fittings with respect to both PFO and EXP models, as testified by its lower values of the error functions computed for each analysed liquid–solid system. For PSO model, k_{PSO} turns out to be on the order of 10^{-4} – 10^{-3} g mg⁻¹ min⁻¹, depending on the sorbent. On the other hand, each fractal kinetic model determines a more reliable adsorption dynamic prediction when compared to its classical formulation, as confirmed by the lower values of the HYBRID function, which is a more suitable statistical criterion for discriminating among regression models including a different number of fitting parameters [25]. Among fractal-like kinetics, the FPFO appears to be the most adequate model to describe cadmium adsorption in almost all the investigated cases; for SG10 the FEXP model is slightly more accurate than the FPFO one, but differences between the statistical error functions are not so marked. For FPFO model, k'_{FPFO} turns out to be on the order of 10^{-3} – 10^{-2} min^{-(1-h)}, with $h = 0.27$ – 0.66 , depending on the

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