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What can the use of well-defined statistical functions of pollutants sorption kinetics teach us? A case study of cyanide sorption onto LTA zeolite nanoparticles

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HIGHLIGHTS

- LTA zeolite was successfully synthesized and used as a sorbent for the cyanide.
- Kinetics data are clearly described by the Brouers-Sotolongo ($BSf(n,\alpha)$) model.
- Two principal fractal models $BSf(n,\alpha)$ and fractional derivative have been compared.
- $BSf(n,\alpha)$ model was extended and improved using a time-dependent coefficient.
- The Elovich model was found to be incorrectly used in several studies.

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ABSTRACT

This study demonstrates that the introduction of a fractal time yields a more clear description of the kinetics in the case of the aqueous phase sorption of cyanide onto LTA zeolite nanoparticles. The two best-known fractal models, the Brouers-Sotolongo ($BSf(n,\alpha)$) fractal model and kinetics formula based on the Riemann–Liouville fractional derivative theory, are compared. These two models give very similar results and we present arguments for our preference for the former one. Another commonly employed model, the Elovich equation, is discussed. We justify that its continued use in its approximate form is currently not required, as it is inaccurate particularly for small uptake. Its exact expression produces results similar to the two former ones only for part of the kinetics curve, but it is unsuitable as it asymptotically yields an infinite value of the uptake. Besides, an extension of the $BSf(n,\alpha)$ is proposed by introducing a time-dependent fractal coefficient, which more clearly explains the evolution of the kinetics in detail and enables a more accurate calculation of the time-dependent rate, typical of non-exponential kinetics. The results reveal that, in this particular case of cyanide sorption onto zeolite, this model is the best fit to the experimental kinetics data.

1. Introduction

At present, the rapid rise in the rate of aquatic environment contamination, with the inflow of toxic substances like cyanide, has become one of the major environmental concerns and has drawn the attention of researchers and engineers who

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are diligently seeking effective techniques to treat the industrial effluents released into water bodies, and ensure they are maintained within the acceptable limits for contaminants (Giraldo and Moreno-Pirajᾶn, 2010). Cyanide, a material ranking high on the Hazardous Substance List, poses a serious threat to human and other life forms. Humans chronically exposed to cyanide primarily exhibit its detrimental effects on the central nervous system (USEPA, 2010). Cyanide also affects the cardiovascular and respiratory systems, inducing thyroid gland enlargement, as well as eye and skin irritation (Dash et al., 2009). Several studies have demonstrated that the sorption technique is effective in sequestering the cyanide from contaminated water (Samarghandi et al., 2015; Sulaymon et al., 2014; Mohammed et al., 2016). As this treatment appears to be economically attractive and simple, it is extensively used in wastewater treatment (Yazici et al., 2009). One of the tasks facing environmental scientists is to study the effectiveness and reliability of various materials for the sorption of organic and inorganic materials from polluted aqueous environments. Nano-materials have recently drawn wide attention in this field, for their high surface area and excellent mechanical properties. For instance, nano-sized Linde Type-A (LTA) zeolite materials have attracted much interest in adsorption applications and proven to be an excellent adsorbent for the removal of several hazardous chemicals from aqueous solutions (Samarghandi et al., 2015; Mohseni-Bandpi et al., 2016). The LTA zeolite has been thoroughly investigated for its removal capacity of many pollutants. It was also found to be efficient as an adsorbent for cyanide removal and therefore, is a promising novel application in cyanide elimination from the tertiary stage in wastewater treatment (Noroozi et al., 2018).

The sorption process itself is dependent on the topology of the sorbent surface, energy distribution of the sorbing sites, and physical or chemical nature of the interaction between the pollutant molecules and the sorbing sites on the sorbent. It is obvious that all these features cannot be introduced in detail in the theoretical model because of the heterogeneity of all these factors. Therefore, as the field of sorption must be treated keeping in mind its specific concepts and mathematical methods, it poses quite a challenge for the practitioners, which can be overcome only through interdisciplinary collaborations.

It is imperative to be able to predict the sorption kinetics rate and maximum quantity of pollutant removed from the aqueous solutions in order to design and scale-up a suitable adsorption treatment system (Tan and Hameed, 0000). Sorption kinetics explains a time-dependent solute uptake which, in turn, controls the residence time of the sorbate uptake at the solid–solution interface. This highly complex process is a phenomenon involving three steps, based on the nature of the sorbent–sorbed couple and external conditions (temperature, pH, concentration of pollutants, etc.). The sorbed molecules need to first diffuse into the external film, then enter the pores until they reach the sorbing center after which the surface reaction occurs, which is the actual attachment process of the adsorptive molecules to the active sites on the sorbent surface. These three steps include mass transfer dependent upon the surface heterogeneity, pore structure and distribution of sorbing energies, which are either chemical or physical in nature. The equilibrium state thus achieved is the result of a birth-and-death mechanism involving the sorption and desorption processes. Evidently, a detailed microscopic or macroscopic model cannot be derived and it is impossible to incorporate all the details involved in these successive processes. The time dependence of the uptake is determined only by experimentation. In order to appreciate the evolution of the kinetics, statistical and stochastic methods are utilized which, hopefully, on the macroscopic level, will provide pertinent parameters characterizing each system, and which can be applied in light of industrial applications. This mathematical problem, based on statistical and stochastic theories, bears some similarity to the relationship between microeconomics and macroeconomics; therefore, it will not come as a surprise that some of the methods proposed here are derived from econometrics.

A sizable number of the papers published over the last decades in the field of adsorption kinetics have interpreted their findings utilizing pseudo-first-order or pseudo-second-order kinetic models (Bulut and Aydin, 2006; Yuh-Shan, 2004; Ho and McKay, 1998). Furthermore, the Elovich kinetic model has been applied to chemisorption on a heterogeneous surface (Wu et al., 2009; Al-Musawi et al., 2017). Although the traditional kinetic pseudo-first-order and pseudo-second-order equations can at times give a good fit with the coefficient of determination or correlation function (R^2) values >0.995, as is the case in the current study, we cannot be satisfied with an equation that fails to yield the correct time variation in the rate and which masks the true evolution of the kinetics whose rate is not necessarily constant (pseudo-first-order), linear (pseudo-second-order), or monotonous (monotonous behavior occurs when a function always increases or decreases; non-monotonous behavior means that the function decreases and then increases or *vice versa*). However, it is very well documented in the literature, as mentioned earlier, that the overall adsorption in a porous adsorbent must consider the adsorption rate on an active site, as well as the external mass transfer, surface diffusion, intraparticle diffusion and pore volume diffusion (Karapanagioti et al., 2001; Ho and McKay, 1998). A paper published recently, criticizes some of the automatic empirical routine methods employed to model the adsorptive removal of pollutants in an aqueous phase and has reviewed the recent efforts to provide a more precise framework to that field (Tan and Hameed, 0000). These authors emphasized the poor data furnished by the routine fitting using pseudo-first-order and pseudo-second-order equations. Further, they insisted that the non-linear fitting and introduction of a fractal time in the equation facilitates a clearer understanding of the evolution of the sorbing process, as well as gives clues regarding the physical and chemical mechanisms responsible for it.

The objective of this paper is to use the same nonlinear fitting and fractal kinetic models, as well as critically investigate the methods used to interpret the kinetic curves which are used to characterize the sorption process and the sorbing capacity of these materials; these curves are significant at the moment of their selection for practical applications. Besides, the present study has reviewed some of the more popular statistical functions, rather than the usual empirical formulae which have been used, to extend beyond the classical pseudo-first-order and pseudo-second-order kinetic models and presented some new developments of the Brouers-Sotolongo fractal theory.