Research article

Degree of time dependency of kinetic coefficient as a function of adsorbate concentration; new insights from adsorption of tetracycline onto monodispersed starch-stabilized magnetic nanocomposite

Chukwunonso P. Okoli [a, b, *], Augustine E. Ofomaja [a]

[a] Department of Chemistry, Vaal University of Technology, P. Bag X021, Vanderbiljpark, 1900, South Africa
[b] Department of Chemistry/Biochemistry & Molecular Biology, Federal University, Ndufu Alike Ikwo (FUNAI), Ebonyi State, Nigeria

ABSTRACT

The realization that the observed kinetic coefficient (k_{obs}) varies with time in most real-time adsorption system, as against the constant value conceived in the most widely-applied adsorption kinetic models, have attracted much attention in recent time. Understanding the factors that control the extent/degree of time dependency (otherwise known as fractal-like kinetics), is therefore central in taking manipulative advantage of this phenomenon in critical adsorption applications. This study therefore deployed non-fractal-like and fractal-like kinetic approach to study the adsorption of tetracycline on monodispersed starch-stabilized magnetite nanocomposite (MSM). MSM was synthesized by in-situ coprecipitation of magnetite in the presence of starch, and successfully characterized with classical solid-state techniques. Isotherm studies indicated that MSM has heterogenous surface adsorption sites. Equilibrium and kinetic data indicated the existence of π-cation interaction as the underlying mechanism, while pH study revealed that tetracycline was adsorbed in its zwitterion form. Though the non-fractal kinetic models exhibited some level of relevance in explaining the tetracycline adsorption interactions, the best fitting of the fractal-like pseudo second order model to the adsorption kinetic data, indicated that the real-time adsorption kinetics occurred in fractal-like manner. The study also revealed that the degree of time dependency of k_{obs} had negative correlation with the initial tetracycline concentration. Apart from developing a low-cost strategy for addressing tetracycline water pollution, the result of this study serves a positive step towards gaining manipulative control of adsorption mechanism in potential application of MSM for targeted drug delivery and controlled release of tetracycline antibiotics.

1. Introduction

Magnetic polymer nanoparticles have gained increasing attention due to its desirable qualities and increasing proven and potential applications. The driving concept on the design of magnetic polymer nanocomposite is the expectation that combination of magnetic nanoparticles with polymers offers the opportunity to develop composite materials that combine the properties from the individual components (Philippova et al., 2011). Among other magnetic materials for synthesizing magnetic polymers, magnetite nanoparticles have proved to be the most widely accepted candidate, due to their biocompatibility, low toxicity and superparamagnetic character (Ito et al., 2005). In recent times, the magnetic polymers that incorporate natural polymers such as proteins and polysaccharides have attracted much attention due to their biodegradability, non-toxicity, low cost and ability to form hydrogels with myriads of proven and potential applications (Berry and Curtis, 2003; Hong et al., 2008). Starch has attracted higher attention than other natural polymers due to the fact that apart from its biocompatibility and availability at relatively low cost, starch is amenable to a variety of chemical modifications like substitution, grafting, cross-linking reactions etc., to produce materials with novel properties (Kaewtatip and Thongmee, 2013; Okoli et al., 2014a, 2015, 2016).

Among the various applications of magnetic polymer nanoparticles (Kalia et al., 2014), targeted drug delivery, controlled release of pharmaceutically active compounds and treatment of chemical water pollution, are the potential applications where adsorption is the fundamental principle of operation/application. Basic understanding of the principles of operation of these

applications serves as a vital guide for assessing the suitability of any materials. In all the adsorption-based applications, the material must have affinity for the adsorbates of interest. However, while adsorption process for water treatment does not need manipulation of the physicochemical properties for the release of the adsorbates of interest, targeted drug release requires loss of the entire affinity under certain condition, whereas controlled release demands for controlled reduction in the affinity of the material for the adsorbates of interest, over time. Since the affinity of adsorbents for adsorbates is a function of adsorption mechanism, understanding the mechanism of an adsorption process is crucial for assessment and/or utilization of any material for adsorption based potential applications (Okoli et al., 2014b; Ji et al., 2009). Establishment of fractal-like nature of adsorption has been applauded as great step towards gaining manipulative control of adsorption mechanism (Kopelman, 1988; Azizian and Fallah, 2010; Haerifar and Azizian, 2012, 2014). However, while the time dependent nature of adsorption coefficient has dominated recent literature on fractal-like kinetic studies, little is known on the factors/parameters that influence the degree of time dependency of its values, and their subsequent manipulative advantage in adsorption applications.

It has been established that antibiotics are the most rampant amongst the pharmaceutically active compounds detected in water environment, due to their widespread applications in human health and livestock management (Liu et al., 2017). Amongst the antibiotics, the effective antimicrobial actions and lack of established major adverse side effects have given tetracycline an edge over other antibiotics drugs. Thus tetracycline have been extensively administered in human medicine as well as livestock production for disease control, and as feed supplement at sub-therapeutic levels to improve feed efficiency, growth rate, and general health (Zhang et al., 2014a). Despite the fact that the levels of tetracyclines found in most water media are below the thresholds required to exhibit minimum inhibitory concentration (MIC) for medical benefits, they still exert pressure on the evolution of antibiotic resistant bacteria which in turn may minimize the effectiveness and therapeutic value of antibiotics (Ehlert, 2010). This situation can obviously impact negatively on public health when human beings are exposed to these resistant microbes. Due to their relative persistence in aquatic environment, these pharmaceutically active compounds also pose long-term risks to aquatic life and their dependents through endocrine disruption. Hence, there is an obvious need to develop efficient abatement strategy.

Review of previous efforts in adsorption removal of tetracycline from aqueous media revealed a series of draw-backs that has limited the utilization of adsorption technology as a water treatment option for addressing pharmaceutical water pollution (Priya and Radha, 2017). These adsorbent based challenges are mainly emanating from non-availability of effective/efficient adsorbents, non-biodegradability of available adsorbents, and inhibitory cost of adsorbents. Aside improvement in adsorption efficiency, utilization of magnetic polymer nanocomposite enhances deployment of magnetic separation (Okoli et al., 2018). This eliminates the separation challenge encountered with nanoscale adsorbents which often form colloidal suspension/emulsion, and ultimately enhance operation cost reduction. The present study is therefore designed to utilize monodispersed starch stabilized magnetite nanoparticle for removal of tetracycline antibiotics from aqueous media. As the role of adsorption mechanism cannot be over-emphasized in assessing any adsorption-based application of any material, the present study therefore deployed the fractal-like approach to gain new insights on the time dependency of the kinetic coefficient, investigate the factors/parameters that influence the degree of dependence, and overall mechanism of tetracycline adsorption on starch stabilized monodispersed magnetite nanocomposite. Apart from developing

a low-cost strategy for addressing tetracycline water pollution, the result of this study is expected to serve as a guide for assessing the potential application of starch stabilized magnetite for targeted drug delivery and controlled release of tetracycline antibiotics.

2. Theoretical concept

The concept of time dependency of reaction kinetic coefficient in homogeneous phase was proposed by Kopelman (1988) and then developed for adsorption by Haerifar and Azizian (2012, 2014); Bashiri and Shajari (2014). In a different approach, Brouers and Sotolongo-Costa (2006); Brouers (2014); Brouers and Al-Musawi (2018) showed that the empirical formula for fractal-like kinetics stems from approximations of a well-defined mathematical and statistical expression named Brouers-Sotolongo kinetics, which has attracted increasing attention for modelling liquid-phase adsorption kinetics (Al-Musawi et al., 2017; Selmi et al., 2018). Though normal empirical kinetic models have been successful in giving physical meaning to adsorption kinetic data and exploration of adsorption mechanisms in adsorption systems, the concept of fractal like kinetic modelling has brought a new insight in the interpretation of adsorption kinetics data. While the normal empirical kinetic model concept approximates the adsorption kinetic coefficient to a constant value throughout the adsorption process, the fractal-like kinetic approach is propounded on the basis that the value of kinetic coefficient is time dependent. Fractal-like kinetics postulates that the observed rate coefficient k_{obs} (instantaneous) is not a constant parameter, but it rather decreases by passing time as a fractal-like or time dependent parameter, as captured in eq. (1).

$$k_{obs} = k't^{-h}(0 \leq h \leq 1)(t \geq 1) \tag{1}$$

where k' is the rate coefficient at time $t > 0$ (t strictly positive), and h is a constant parameter related to the extent of time dependency of the kinetic coefficient.

All the fractal-like kinetic equations have been derived by conceptual and mathematical transformation of equation (1). Haerifar and Azizian (2012) derived a fractal-like kinetic equation for homogeneous surfaces, and linked the fitting of kinetic data to their equation as an indication of possibility of different paths for molecules to be adsorbed on the surface sites by passing of time, despite having sites of identical energy. As most surfaces are often of heterogeneous nature, fractal-like kinetic equations have recently been derived for heterogeneous surfaces (Haerifar and Azizian, 2014). Considering the wide application of adsorption in various fields, the extent of time dependency of the kinetic coefficient, is obviously important in assessing the suitability of materials for various applications. For instance, improved understanding of the time dependency of kinetic coefficient will confer the desired manipulative control of drug delivery in targeted/control drug delivery applications, in view of the highly sensitive nature of human health system. Obviously, the insights from fractal-like approach are expectedly more far reaching than the normal empirical models.

Despite having different fractal-like kinetic equations for homogeneous and heterogeneous surfaces, the fitting of a kinetic data to respective fractal-like models is not a sufficient means of surface energy characterization. However, following of adsorption kinetic data with fractal-like models for homogeneous surfaces gives insight on the presence of different paths for adsorption, while following the fractal-like kinetic model for heterogeneous surfaces gives insight on the nature of the different adsorption sites and their respective affinity for adsorption. So, at first instance, homogeneous and heterogeneous surfaces are distinguished by use of