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Kinetic models for adsorption on mineral particles comparison between Langmuir kinetics and mass transfer

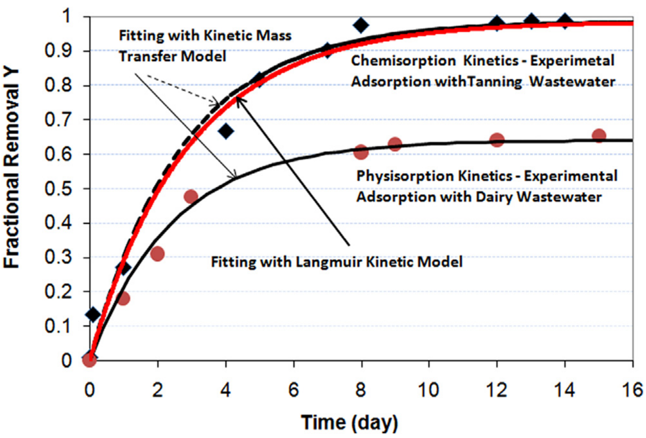
Maher Al-Jabari

Environmental Technology Engineering, Palestine Polytechnic University, Hebron, Palestine

HIGHLIGHTS

- A theoretical model for batch adsorption process based on the Langmuir rate equation is presented.
- A closed form mathematical solution is used to obtain the theoretical adsorption curves.
- The effects of the various adsorption parameters are presented and discussed.
- The model is used to fit experimental results for the adsorption of chromium on stone particles.
- Results obtained from this model are compared to those obtained from a mass transfer model.

GRAPHICAL ABSTRACT



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ABSTRACT

This paper presents a parametric study of kinetic adsorption model, for treating industrial wastewater contaminated with heavy metals by mineral particles, using Langmuir kinetics. It also compares the model with a mass transfer model, as a mathematical limiting case. Theoretical adsorption curves are presented in a simple form of fractional removal of pollutant as a function of time. They are obtained from the mathematical solution of ordinary differential equations, derived from differential mass balance and Langmuir kinetic rate equation. The effects of dimensionless process parameters on the fraction removal are presented. These include: equilibrium constant, particle dosage, ratio of the initial mass of pollutant to the maximum adsorbed mass, and Langmuir rate coefficient. The model provides a good fit to experimental results for adsorption of Cr(III) on both marl stone and stone cutting particles. A simplified fitting approach is presented.

E-mail address: mjabari@ppu.edu.

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Nomenclature

A	A parameter defined by Eq. (15).
B	A parameter defined by Eq. (16).
a	The specific surface area of the sample ($cm^2\ g^{-1}$).
$\bar{c}$	The concentration of the pollutant in the wastewater ($g\ cm^{-3}$).
C	The dimensionless concentration of the pollutant in the wastewater.
c_0	The initial concentration of the pollutant in the wastewater ($g\ cm^{-3}$).
Er	The sum of the deviations squared between the experimental value (Y_{exp}) and the theoretical value (Y).
F	The adsorbent dosage used in treating wastewater ($g\ cm^{-3}$).
f	A function defined in Eq. (14).
K	Langmuir equilibrium constant defined in Eq. (2) ($cm^{-3}\ g^{-1}$).
k_L	The mass transfer coefficient ($cm\ s^{-1}$).
k_1	The adsorption coefficient ($cm^{-3}\ g^{-1}\ s^{-1}$).
k_2	The desorption coefficient (s^{-1}).
$k_L a$	The volumetric mass transfer coefficient ($cm^{-3}\ g^{-1}\ s^{-1}$).
$\bar{q}$	The mass fraction of the pollutant on the adsorbent surface.
q	The dimensionless mass fraction of the pollutant on the adsorbent surface defined in Eq. (6).
Q	The dimensionless mass fraction of the pollutant on the adsorbent surface defined in kinetic mass transfer model as per Eq. (23).
q_m	The maximum mass fraction of the pollutant that can be adsorbed on the solid surface for monolayer coverage.
t	The time (s).
V	The total volume of the extraction vessel (cm^3).
Y	The fraction removal of the pollutant, defined in Eq. (19).
Y_e	The equilibrium fraction removal of the pollutant from wastewater.
Y_{exp}	The experimental fractional removal of the pollutant at any time.

Greek letters

ε	The volume fraction which is occupied by the wastewater phase in the adsorption vessel.
ϕ	The ratio of the initial mass of the pollutant in wastewater to the maximum mass than can be accommodated on the solid surface for monolayer coverage.
ρ_s	The density of the adsorbent ($g\ cm^{-3}$).
τ	The dimensionless time, defined in Eq. (17).

1. Introduction

Adsorption is one of the most important treatments in the environmental field. It has a wide range of applications in wastewater treatment. Types of pollutants in industrial wastewaters include organics, chemicals, and heavy metals ...etc. (Crini, 2005). Chromium is one of the major pollutants in industrial wastewater. It is encountered in two oxidation states: Cr^{3+} (e.g. from leather tanning) and Cr^{6+} (e.g. from galvanization surface treatment). Hexavalent chromium is toxic.

Adsorption studies were concerned with equilibrium experimentation and modeling, as well as kinetic studies. Kinetic models handle fixed bed adsorption columns (Xu et al., 2013; Shafeeyan et al., 2014) and batch adsorption processes (Hameed et al., 2009; Imaga and Abia, 2015; Ahmad et al., 2007; Mittal et al., 2015; Demirbas et al., 2004; Ho and McKay, 1998; Cruz et al., 2004; Karaca et al., 2004; Wang and Li, 2007; Hameed and El-Khaiary, 2008; Güzel et al., 2015; Ho, 2006). This paper is limited to kinetic models for batch adsorption.

Adsorption is a surface phenomenon that occurs by two main mechanisms: chemisorption and physisorption, depending on the characteristics of the adsorbent surface and adsorbate. In tanning wastewater treatment (and in similar industrial applications), the pollutants are heavy metals. Thus, the adsorption is believed to be of a chemical type; it is controlled by the interactions at the surface of the adsorbents.

The author and his co-workers utilized the concept of treating waste-by-waste, and handled the chemical adsorption of trivalent chromium onto various mineral particles of stone cutting solid waste, marlstone, and soil (Al-Jabari et al., 2012, 2009a,b). In addition, physical molecular adsorption of organic pollutants from dairy wastewater onto the same mineral particles were investigated experimentally (Al-Jabari et al., 2015). A mass transfer model was developed by the author for batch physisorption (Al-Jabari, submitted for publication). A kinetic model is required for chemisorptions, which takes into account the interactions between the pollutants and the surface of adsorbents.