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Use of refuse-derived fuel waste for the adsorption of 4-chlorophenol and dyes from aqueous solution: Equilibrium and kinetics

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ABSTRACT

Porous carbons with surface area of 898 and 1461 $m^2 g^{-1}$ were prepared from refuse-derived fuel (RDF-5) waste via NaOH activation at 780 °C and a NaOH/char weight ratio of 1 (RDFN1) and 2 (RDFN2), respectively. Changes in surface morphology and chemical compositions of the carbons were studied by SEM and elemental analysis. The ability of these carbons for the adsorption of 4-chlorophenol (4-CP), acid blue 74 (AB74), and methylene blue (MB) from aqueous solution were examined. Various isotherm (Frenudlich, Langmuir, and Sips) and kinetic (pseudo-first-order, pseudo-second-order, and Elovich) equations were fitted by nonlinear regression using SigmaPlot 11 software. It was shown that the pseudo-second-order equation best described adsorption of 4-CP and AB74 on RDFN2, whereas Elovich equation best followed adsorption of three solutes on RDFN1. The similarity index between the Sips and Langmuir or Freundlich equations was finally proposed from isotherm parameters obtained based on 59 adsorption systems.

1. Introduction

The densified refuse-derived fuel (RDF-5) is convenient for transportation and storage, high in calorific value, and low in pollution. In 2005, the production of RDF-5 waste reached 13 million tons in EU, indicating the rapid development of RDF-5 waste as an alternative energy source. The use of RDF-5 in Asia is gradually becoming popular, *e.g.*, in Japan and Taiwan [1]. In our previous study [2], highly porous carbons with a surface area of 1655 $m^2 g^{-1}$ were obtained from RDF-5 waste *via* KOH activation; however, alkaline activation by NaOH is cheaper, less corrosive, and more environmentally friendly than by KOH [3]. Moreover, NaOH-activated carbons exhibited a high adsorption capacity for dyes and phenols from aqueous solution [4,5].

Freundlich equation, originally proposed in 1906 [6], has been used for a hundred years but was still subjected to many descriptions and questions [7]. In spite of criticisms, Freundlich equation is one of the most widely used adsorption isotherms. On the other hand, Langmuir equation, suggested in 1918 [8], describes the surface as homogeneous assuming that all adsorption sites have equal solute affinity and that the adsorption at one site does not affect adsorption at the adjacent site [9]. Although only few adsorption systems meet these conditions, many processes were described by Langmuir equation due to its convenience in linear curve-fitting. The above two equations have been often used in engineering calculations; however, the parameters provided from different equations yield large difference in process design applications and cause users confused. Before computer era, the linear curve-fitting results of both equations could not provide overall picture of the adsorption processes. In general, Freundlich equation is more suitable in the lower ranges of solute concentration, whereas the fit of Langmuir equation is more suitable in higher concentration ranges [10].

Nowadays, computer calculation and statistics are applied to carry out complicated nonlinear regression and to confirm the fitting by isotherm Eqs. [11–23]. However, every equation has its characteristic curves and differences between the curves derived from Freundlich and Langmuir equations are generally large [2,24,25]. These two equations are hard to simultaneously describe the data well. In this regard, the three-parameter Sips equation that combines Freundlich and Langmuir hypothesis is worth

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Notation

C_0	initial liquid-phase solute concentration ($\mathrm{g/m^3}$)
C_e	liquid-phase solute concentration at equilibrium defined in Eq. (16) ($\mathrm{g/m^3}$)
C_t	liquid-phase solute concentration at time t ($\mathrm{g/m^3}$)
D_p	average pore diameter (nm)
F	statistic gauges contribution of independent variables in predicting dependent variable
K_F	parameter of Freundlich equation defined in Eq. (1) $(\mathrm{g/kg})\,(\mathrm{m^3/g})^{1/n_F}$
K_L	parameter of Langmuir equation defined in Eq. (4) ($\mathrm{m^3g}$)
K_S	parameter of Sips equation defined in Eq. (7) $(\mathrm{m^3/g})^{1/n_S}$
N	number of data points
n_F	parameter of Freundlich equation defined in Eq. (1)
n_S	parameter of Sips equation defined in Eq. (7)
P	probability of being wrong in concluding that there is an association between dependent and independent variables
q_e	amount of adsorption at equilibrium defined in Eq. (16) (g/kg)
$q_{m,L}$	amount of monolayer adsorption based on the Langmuir equation defined in Eq. (4) (g/kg)
$q_{m,S}$	amount of adsorption derived from the Sips equation defined in Eq. (7) (g/kg)
q_t	amount of adsorption at time t defined in Eq. (17) (g/kg)
r^2	coefficient of determination
SE	standard error of the estimate by equation defined in Eq. (17) (g/kg)
S_{micro}	surface area of adsorbent due to micropores ($\mathrm{m^2/g}$)
S_p	BET surface area of adsorbent ($\mathrm{m^2/g}$)
t	time (min)
u	parameter of Elovich equation defined in Eq. (14) (g/ (kg/min))
v	parameter of Elovich equation defined in Eq. (14) (kg/g)
V	volume of liquid phase ($\mathrm{m^3}$)
V_{micro}	pore volume due to micropores ($\mathrm{cm^3/g}$)
V_p	total pore volume ($\mathrm{cm^3/g}$)
W	weight of dried adsorbent (kg)

testing [26]. As Sips equation is used to fit the data, the least error is obtained. Previous studies indicated that Sips equation describes adsorption isotherms more accurately than both individual Eqs. [27–34]. The characteristic curves of Sips equation will be thus constructed to explain its ability of describing a wider range of solute concentration in adsorption processes.

In this work, RDF-5 waste was activated by NaOH to prepare carbonaceous adsorbents, and the adsorption isotherms and kinetics for 4-chlorophenol (4-CP), acid blue 74 (AB74), and methylene blue (MB) were studied. The commercial software SigmaPlot 11, which involves the corresponding forms of isotherm equations in its equation category, was used to perform nonlinear regression. This is because this software can readily provide not only the regression results of isotherm and kinetic parameters but also the statistical error analysis results including r^2 (coefficient of determination), SE (standard error), F-test, and P values. These statistical data enable us to understand the errors existing in each equation. According to regression results of a group of adsorption systems reported earlier, the similarity indices between the Sips and Langmuir or Freundlich equations were proposed. Fitting pseudo-first-order (PFO), pseudo-second-order (PSO), and Elovich equations to kinetic data was similarly performed by applying regression procedures.

2. Theoretical backgrounds

2.1. Linear and nonlinear regression forms of Freundlich equation

Freundlich equation basically describes the adsorption equilibrium between a solute in the solution and the surface of adsorbent, using a multi-site and multi-layer concept for heterogeneous surfaces [35]. The nonlinear form of Freundlich equation is given by

$$q_e = K_F C_e^{1/n_F} \tag{1}$$

where q_e is the amount of adsorption at equilibrium (g/kg), C_e is the liquid concentrations at equilibrium ($\mathrm{g/m^3}$), K_F is the Freundlich constant related to adsorption capacity $(\mathrm{g/kg})(\mathrm{m^3/g})^{1/nF}$ and $1/n_F$ is the constant related to adsorption intensity.

The corresponding form in the equation category of SigmaPlot 11 “Power, 2 Parameter” is expressed by

$$y = ax^b \tag{2}$$

The corresponding parameters are $y = q_e$, $a = K_F$, $b = 1/n_F$, and $x = C_e$.

The linear form of Freundlich equation is:

$$\ln q_e = \ln K_F + \left(\frac{1}{n_F}\right)\ln C_e \tag{3}$$

Eq. (3) highly complies with adsorption process in lower concentration range and is often used in engineering practice. However, the parameters of Eq. (3) are obtained from linear regression of ln q_e vs. ln C_e but not from the best-fit curve of q_e vs. C_e; the difference between these two items has been indicated [11]. In Section 4.3, nonlinear Eq. (1) will be discussed.

2.2. Linear and nonlinear regression forms of Langmuir equation

Langmuir theory describes the monolayer coverage of solute on a homogeneous adsorbent surface. The isotherm is based on the assumption that adsorption occurs at specific homogeneous sites within the adsorbent, and that once a solute molecule occupies one site no further adsorption can take place at that site [35]. The nonlinear form of Langmuir equation is written as:

$$q_e = \frac{K_L q_{m,L} C_e}{1 + K_L C_e} \tag{4}$$

where K_L is the Langmuir constant ($\mathrm{m^3/g}$) and $q_{m,L}$ is the amount of adsorption corresponding to monolayer coverage (g/kg).

The corresponding form in the equation category of SigmaPlot 11 “Hyperbola equation, Modified Hyperbola I” is given by

$$y = \frac{ax}{1 + bx} \tag{5}$$

The corresponding parameters are $y = q_e$, $a = K_L q_{m,L}$, $b = K_L$, and $x = C_e$.

The linear form of Langmuir equation is expressed by:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{m,L}} + \left(\frac{1}{q_{m,L}}\right)C_e \tag{6}$$