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Research Paper

Adsorption of dibenzothiophene by walnut shell-activated carbon/chitosan/iron nanocomposite: kinetics, equilibrium, thermodynamics and mass transfer modeling

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1. ABSTRACT

In this research, activated carbon was prepared by chemical activation from walnut shells, then modified by iron nanostructure and chitosan separately and together, and used to remove dibenzothiophene from isooctane fuel. The BET and EDX-SEM analyses were used to investigate the adsorbent properties. Equilibrium experiments showed that the adsorption process is a single layer, and the maximum adsorption capacity is 285.71 and 178.57 mg/g for AC_1 and AC_2, respectively. The results of kinetic data showed that the pseudo-second-order kinetic model is consistent with the experimental result. To determine mass transfer parameters, the mathematical model of film-pore-surface diffusion model was used by MATLAB software and it was observed that external mass transfer and pore diffusion stages are more important.

Keywords: Adsorption, Walnut Shell-Activated Carbon, Isooctane, Dibenzothiophene, Modeling.

2. INTRODUCTION

The process of adsorption around the solid particle (adsorbent) takes place during the following stages: bulk diffusion, film (external) diffusion, internal diffusion, and surface adsorption [1, 2]. One of the most popular adsorbents is activated carbon, which is known as a high-capacity adsorbent due to its high specific surface area, porous structure, and high mechanical and chemical resistance. Various methods have been proposed for improving the capacity and adsorption ability of activated carbon, including the use of biopolymers and nanostructures [3]. The aim of this research is the synthesis of activated carbon (AC) from walnut shell and the modeling of the mass transfer process of surface adsorption of di-benzothiophene (DBT) from isooctane liquid fuel model with iron functionalized activated carbon (AC_1) and iron/chitosan functionalized activated carbon nanocomposite (AC_2).

3. MATERIALS AND METHODS

3.1. Preparetion of activated carbon and its functionalization

Activated carbon was synthesized from walnut shell using phosphoric acid as an activator according to the method presented in reference [4]. Chitosan was prepared from shrimp shells according to the method presented in reference [4]. In order to modify AC with iron groups, first, 5 g of AC was added to 2 M iron chloride solution, and the resulting mixture was then sonicated for 60 minutes at 25 °C. Then, the iron-functionalized activated carbon (AC_1) was washed several times with distilled water. The iron/chitosan functionalized activated carbon nanocomposite (AC_2) was synthesized according to the method presented in reference [4]. AC, AC_1, and AC_2 were characterized using BET and SEM-EDX analyses.

3.2. Adsorption experiments

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Kinetic experiments were performed at an initial concentration of 100 mg/L with 2 g/L of adsorbent for a period of 5 to 360 minutes for AC_1 and AC_2 adsorbents. Equilibrium tests were also carried out for both adsorbents with 2 g/L of adsorbent and a contact time of 24 hours at initial concentrations of 50-300 mg/L. The concentration of DBT in the solution was determined using a UV-vis device.

3.3. Modeling of adsorption process

In this study, a mathematical model including internal diffusion (pore and surface diffusion) and external (film) diffusion called the film-pore-surface diffusion model (FPSDM) is presented, and the pore diffusion coefficient D_p (m^2/s), surface diffusion coefficient D_s (m^2/s), and external mass transfer coefficients k_f (m/s) were determined. The mathematical relationships of this mass transfer model and the assumptions considered are presented in the reference [2]. These equations were solved using coding by MATLAB 7.12.0 software (R2011.A).

4. RESULTS AND DISCUSSION

4.1. Characterization of adsorbents

The results of BET analysis showed that the AC, AC_1, and AC_2 adsorbents have a specific surface area equal to 1223 m^2/g, 1181 m^2/g, and 950 m^2/g, respectively. The data show the porous structure of the synthesized adsorbents. According to this data, the modification process by iron and chitosan has reduced the specific surface area of AC, which can be attributed to the blocking of pores by chitosan and iron nanostructures formed on its surface. The average pore diameter (nm) of AC, AC_1, and AC_2 adsorbents was 2.883, 2.901, and 2.588, respectively which is in the appropriate range for DBT adsorption (in the range of 1 nm) due to the molecular size comparable to small pores. The SEM images of AC_1 and AC_2 adsorbents, and EDX spectra of AC, and AC_2 adsorbers are presented in Figure 1, which shows the presence of iron and increasing the amount of nitrogen in the structure of AC_2 in comparison with activated carbon.

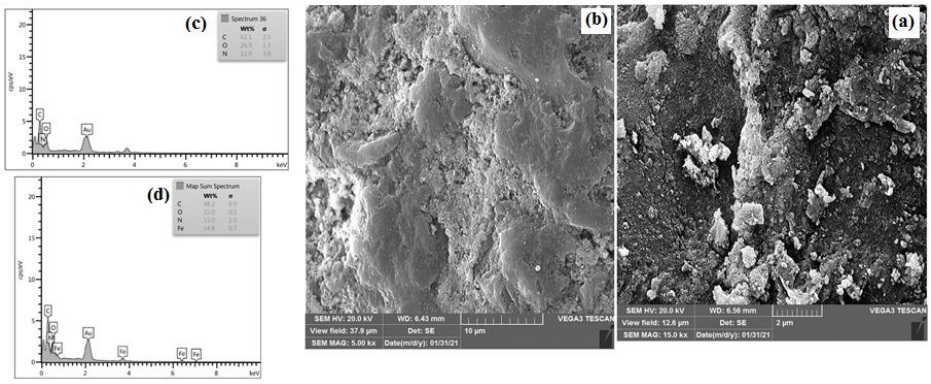

Figure 1. SEM images of (a): AC_1; (b): AC_2; The EDX spectra of (C): AC; (D): AC_2

4.2. Kinetics and equilibrium study

The kinetics data was studied by three kinetic models including pseudi-first and pseudo-second order and intra-particle diffusion models whose equations are presented in reference [4]. The quantities of constant parameters and R^2 for these models are shown in Table 1. The R^2 values for AC_1 and AC_2 adsorbents are the highest values for the second-order model and indicate the compatibility of this model with the experimental data. This shows that chemical adsorption is a more dominant mechanism than physical adsorption, and the adsorption rate depends on the number of surface adsorption sites.

Table 1. The kinetics model parameters for DBT adsorption

Pseudo-first order model			Pseudo-second order model			Intra-particle model			Adsorbent
k_1 (min^{-1})	q_e (mg g^{-1})	R^2	k_2 (g mg^{-1} min^{-1})	q_e (mg g^{-1})	R^2	k_{id} (mg g^{-1} $min^{-1/2}$)	θ	R^2	
0.012	2.183	0.90	0.0203	49.54	1	0.124	47.1	0.96	AC_1
0.008	0.530	0.96	0.085	49.01	1	0.035	48.4	0.90	AC_2

The equilibrium data was studied by three isotherm models including Langmuir, Freundlich, and D-R isotherm models, and their equations are presented in reference [4]. The R^2 values in Table 2 for these isotherms show that the Langmuir model can describe equilibrium data well. The maximum quantities (q_{max}) (theoretical adsorption capacity) of DBT attracted by AC_1 and AC_2 are 285.71 mg/g and 178.57 mg/g, respectively. The equilibrium experiments were performed in various temperatures (25 ◦C, 35 ◦C, 45 ◦C) and the data was applied

to determine the process's thermodynamics [4]. The results showed that the DBT adsorption process using AC_1 was endothermic and using AC_2 was exothermic. The negative values of the Gibbs free energy changes (-21.59 to -23.42 kJ/mol for AC_1, and -23.38 to -24.40 kJ/mol for AC_2) mean that the DBT adsorption process is spontaneous with both adsorbents.

Table 2. The equilibrium model parameters for DBT adsorption

D-R			Freundlich			Langmuir			Adsorbent
E (kJ mol^{-1})	q_m (mol/g)	R^2	K_F (mg g^{-1} $L^{1/n}$ $mg^{-1/n}$)	n	R^2	K_L(L/g)	q_{max} (mg/g)	R^2	
10.04	0.094	0.76	9.291	1.12	0.915	0.033	285.7	0.97	AC_1
10.04	0.095	0.76	11.465	1.20	0.903	0.068	178.57	0.95	AC_2

4.3. Determination of mass transfer coefficien

The kinetic data of the DBT adsorption process with AC_1 and AC_2 adsorbents at 25 °C were analyzed with the comprehensive model of film-pore-surface diffusion model and the value of RSM (root-mean-square) parameter and mass transfer coefficients for each adsorbent are presented in Table 3. From the comparison of RSM values (Table 3), it seems that the film-pore-surface diffusion model has good accuracy in describing kinetics experimental data of DBT/AC_1 and DBT/AC_2 adsorption systems [2].

Table 3. Mass transfer coefficients and RMS values for DBT adsorption process

Parameters	AC_1	AC_2
k_f (m s^{-1})	3.47×10^{-5}	5.98×10^{-5}
D_p (m^2 s^{-1})	8.59×10^{-8}	1.86×10^{-9}
D_s (m^2 s^{-1})	1.063×10^{-15}	6.8×10^{-16}
RMS	11.2728	8.3248

The smaller external mass transfer coefficient of the AC_1 compared to the AC_2 means the higher resistance of the boundary layer surrounding the adsorbent particle and the lower initial rate of DBT adsorption by this adsorbent. The larger D_p value of AC_1 compared to AC_2 can be caused by the higher specific surface area and porosity of this adsorbent compared to AC_2. Also, when modifying with iron groups, iron functional groups are created on the surface of the adsorbent, which act as adsorption centers for DBT adsorption with Lewis acid-base electrostatic mechanisms. When modifying with chitosan and iron, in addition to these iron adsorption sites, the amino adsorption sites due to chitosan are also created, and these amino groups are also Lewis bases and reduce DBT adsorption by repulsion, and for this reason, the adsorption capacity (q_{max}) and surface diffusion coefficient for AC_2 adsorbent are lower than AC_1 adsorbent.

5. CONCLUSION

In this research, activated carbon (AC) was synthesized from the chemical activation of walnut shell. The synthesized AC was modified by iron functional groups and chitosan (AC_2) and by iron functional groups (AC_1) in order to increase its performance. By examining the results of kinetics data with the various models, the second-order kinetic model was compatible with the experimental data. The Langmuir model showed a higher agreement with the equilibrium data than other models. Therefore, the adsorbent surface is considered homogeneous and single-layer adsorption process. According to thermodynamic calculations, the adsorption process by AC_1 adsorbent is endothermic and the adsorption process by AC_2 adsorbent is exothermic. The mass transfer parameters of AC_1 and AC_2 adsorbents were calculated with the FPSDM comprehensive mass transfer model and it was found that both pore diffusion and surface diffusion stages are important. Considering the order of magnitude of these coefficients, it can be pointed out that the greater importance of pore diffusion can be caused by the high porosity of the applied adsorbents.

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