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2,4-D PESTICIDE ADSORPTION PERFORMANCE OF THE BIOMAGNETIC COMPOSITE

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Abstract

In this study, a global waste was transformed a valuable and useful material by a comprehensive experimental setup. Lentil processing waste-based activated carbon with a high surface area of 1875 m^2/g was synthesized by microwave-assisted K_2CO_3 chemical activation and then successfully converted into a ferrospinel composite. The synthesized ferrospinel composite was applied as an effective adsorbent material in the treatment of 2,4-dichlorphenoxyacetic acid herbicide bearing wastewater. Kinetic modeling of the experimental data obeyed the pseudo-second order model and the equilibrium studies well fitted to the Langmuir isotherm model. The maximum adsorption capacity of the ferrospinel composite towards 2,4-dichlorophenoxyacetic acid was 400 mg/g at 45 ^{0}C. Thermodynamic studies showed the favorability and spontaneity of the adsorption process.

Key words: Lentil processing waste, microwave energy, magnetic composite, copper ferrite nanoparticles, herbicide adsorption

1. Introduction

2,4-Dichlorophenoxyacetic acid (2,4-D) is one of the water soluble herbicide that is widely used in agriculture sector. This most widely used herbicide selectively kills broadleaf weeds by leading uncontrolled growth in them. It can be detected in a lot of commercial grass herbicide mixes, and is widely applied as a weed-killer on cereal plants, grasslands, and fruit gardens. In addition this, over 1.500 herbicide products include 2,4-D as an active component [1]. To World Health Organization (WHO), it is moderately toxic to humans and animals and its maximum concentration is limited with 70 μg/L in drinking water by US Environmental Protection Agency (US EPA) [2]. Besides, 2,4-D has been categorized as carcinogen by US EPA and is doubted to be an endocrine disruptor and it causes sperms immobility, immune insufficiency disorders, kidney and respiratory problems [3]. Therefore, to remove 2,4-D from the environment is a very important issue to be solved. Many methods have been applied to remove 2,4-D from aquatic environment such as advance oxidation [4], photodegradation [5], chemical oxidation with ozone [6], coagulation [7] and adsorption. Of these methods, adsorption is the most preferred and applied due to its ease of operation, low-cost and environmentally friendly features.

2. Materials and Method

2.1. Biowaste and reagents

Lentil processing waste (LW) was suppled as crude biomaterial by a lentil processing factory at Batman in Turkey. $FeCl_3.6H_2O$, $CuCl_2$, K_2CO_3, NaOH, NaCl, HCl and 2,4-dichlorophenoxyacetic

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acid (2,4-D) were bought from Sigma-Aldrich Company.

2.2. Fabrication of LPWAC by microwave-assisted chemical activation with K_2CO_3

In this paper, prior to carbonization process conducted in a tubular furnace, the mixture of the LW and K_2CO_3 was treated with microwave energy (MW) in order to reduce the energy consumption for the chemical activation step. MW heating operations were carried out in a household type microwave furnace (Bosch, Model HMT84G451/36, 2450 MHz). The input power of the MW equipment was set at 900 W and the MW frequency used was 2.45 GHz. Crushed and sieved LPW samples were blended with K_2CO_3 to the wanted activating chemical/precursor ratio (weight of K_2CO_3/weight of LW) in Teflon beakers (100 mL). The K_2CO_3 impregnated samples were immediately subjected to MW treatment for 30 seconds. After that, the MW treated samples were subjected to carbonization.

2.3. Fabrication of the ferrospinel composite

$CuFe_2O_4$ spinel ferrite nanoparticles were loaded to the synthesized optimal activated carbon (LWAC) applying the co-precipitation method by the following procedure: 0.02 mol $CuCl_2$ and 0.04 mol $FeCl_3.6H_2O$ were dissolved in 400 mL distilled water and thereafter 4.8 g of LWAC was added to the this mixture. With severe magnetic stirring, 5 M NaOH was put in drop by drop to increase the mixture pH to round 10. This severe stirring was proceeded for 1 hour. Later on, the mixture was heated to 100 ^{0}C for 2 hours. Then, the prepared magnetic ferrospinel composite was washed with distilled water and separated from water by a simple magnetic procedure. Finally, the synthesized material (FLWAC) was dried at 110 ^{0}C in an oven for 24 hours.

2.4. Herbicide batch adsorption experiments

For the kinetic experiments, the data were obtained at 5-420 min time interval with 250 mg/L initial 2,4-D concentration. For the isotherm studies, 2,4-D initial concentrations ranged from 50 to 600 mg/L and the temperatures were 298, 308 K, 318 K, respectively. The amounts of 2,4-D adsorbed were measured by a UV-visible spectrophotometer (Perkin Elmer Lambda 25) at 282 nm.

3. Results and Discussion

3.1. Kinetic modeling of herbicide adsorption

The 2,4-D adsorption rate on the FLWAC and the possible mechanism were analyzed by applying the experimental kinetic data to the pseudo first-order (PFO), pseudo second-order (PSO) and intraparticle diffusion models. The PFO model proposed by Lagergren [8] is expressed by the following linear equation:

$$log\ q_e = log\ K_F + \frac{1}{n} logC_e \quad (1)$$

The PSO model proposed by Ho and McKay [9] is stated by this linear equation:

$$\frac{t}{q_t}=\frac{1}{k_{ads,2}q_e^2}+\frac{t}{q_t} \qquad (2)$$

where t is the time (min), q_e and q_t (mg/g) are the amounts of 2,4-D adsorbed at time t and equilibrium, respectively. $k_{ads,1}$ (min^{-1}) is the PFO rate constant and $k_{ads,2}$ (g/(mg.min)) is the PSO rate constant.

The kinetic parameters and related correlation coefficients (R^2) that calculated from the linear plots of the PFO and PSO models are reported in Table 1. The PSO model has higher R^2 and closer calculated q_e values ($q_{e,cal}$) to the experimental q_e values ($q_{e,exp}$) than the PFO model. Fitting the PSO model means that the adsorption of 2,4-D onto FLWAC adsorbent has a chemisorption rate-controlling mechanism.

Table 1. Kinetic parameters of the 2,4-D adsorption by FLPWAC composite.

	PFO model			**PSO model**			**W-M model**	
$q_{e,exp}$	$q_{e,cal}$	$k_{ads,1}$	R^2	$q_{e,cal}$	$k_{ads,2}$	R^2	k_{id}	R^2
149.74	112.85	0.011	0.9761	158.73	1.81×10^{-4}	0.9969	3.14	0.9953

3.2. Isotherm modeling and thermodynamics

Langmuir [10] and Freundlich [11] isotherm models which are widely applied to describe adsorption isotherms were fitted to the equilibrium data of 2,4-D onto FLWAC. The linear forms of the Langmuir and Freundlich models are expressed by the following Eq. (3) and Eq. (4), respectively:

$$\frac{C_e}{q_e}=\frac{1}{q_m b}+\frac{C_e}{q_m} \qquad (3)$$

$$\log q_e=\log K_F+\frac{1}{n}\log C_e \qquad (4)$$

where q_m (mg/g) is the maximum adsorption capacity of the adsorbent, b (L/mg) is the Langmuir parameter connected to the adsorption energy. K_F and n are the Freundlich parameters reflects the adsorbent capacity and adsorption intensity, respectively. The isotherm parameters are given in Table 2.

Table 2. Isotherm parameters of the 2,4-D adsorption by FLPWAC composite.

	Langmuir model			**Freundlich model**		
T (K)	q_m	b	R^2	K_F	$1/n$	R^2
298	263.16	0.0101	0.9900	14.79	0.46	0.9840
308	370.37	2.93×10^{-3}	0.9858	4.94	0.63	0.9797
318	400	3.71×10^{-3}	0.9940	7.93	0.56	0.9710

It is observed from the table that, the correlation coefficients support the fact the 2,4-D removal by FLWAC followed the Langmuir model that explains the evenly distribution of the active adsorption sites on the FLWAC surface. The maximal adsorption capacity calculated from the Langmuir model was 400 mg/g at 318 K and this high 2,4-D adsorption capability of FLWAC could be attributed to the high surface area and porous structure of the synthesized AC.
The thermodynamic evaluation of the 2,4-D adsorption onto FLWAC was made using the thermodynamic parameters that calculated from the following equations:

$$In\ K_C = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R} \qquad (5)$$

where K_C is the distribution coefficient ($K_C = q_e/C_e$) for the adsorption, R is the universal gas constant (8,314 J/molK), and T is the absolute temperature (K). ΔH^0 and ΔS^0 are calculated from the slope and intercept of van't Hoff plots of In K_C versus 1/T (Figure not shown). The positive ΔH^0 value (30.99 kJ/mol) shows the endothermic adsorption of 2,4-D. The positive value of ΔS^0 (104.76 J/molK) reveals that while 2,4-D adsorbed onto FLWAC, randomness increased on the surface due to the high affinity of the adsorbent surface to the 2,4-D. Besides, the negative ΔG^0 values (-0.40, -0.82, -2.59 kJ/mol) at various temperatures thereby showing the feasibility and spontaneity of the 2,4-D elimination by FLWAC. In addition to this, more negative values with the rise of temperature point out that the adsorbed quantity of 2,4-D at equilibrium increases with rising temperature and more spontaneous at higher temperatures.

Conclusions

The magnetically separable FLWAC composite was used as a novel 2,4-D herbicide remover in wastewater treatment. The fitness of the isotherm data to the Langmuir model indicated the homogeneous dispersion of the active adsorption centers on the FLWAC surface. The adsorption kinetics of 2,4-D onto ferrospinel composite followed the PSO model. The spontaneous character of the 2,4-D adsorption was supported by negative ΔG^0 values which showed the absence of an energy hindrance for the adsorption process.

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