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Experimental and CFD modeling of diazinon pesticide removal using fixed bed column with Cu-modified zeolite nanoparticle

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ABSTRACT

In this study, perlite was employed as a low-cost source of Si and Al in the synthesis of sodalite zeolite by means of the hydrothermal synthesis method. The structural characterization of this zeolite was performed by XRD, SEM and FTIR analysis. Nanoparticles of Cu_2O (30–60 nm) were loaded on the zeolite and utilized as an adsorbent to remove diazinon in fixed bed column. The SEM-EDX of modified zeolite indicates that the amount of copper loading on the zeolite was 4.5 wt.%. The potential parameters effects such as flow rate (0.5, 1 and 1.5 mL/min), initial concentration (50, 75 and 100 mg/L) and bed height (5–15 cm) were investigated on the column performance. A general model was used to predict the breakthrough curves of the fixed bed for diazinon sorption, given the external mass transfer resistance and the axial dispersion with non-linear adsorption isotherm. COMSOL software was employed for the numerical calculation of equations in the model. There was a good agreement between the predicted theoretical breakthrough curves and the experimental results.

1. Introduction

Currently, pesticide pollution in soils, ground water and surface water is considered an important concern across the world due to the fact that many of such compounds are harmful to both human health and the environment [1]. Organophosphate pesticides are among insecticides with widespread application in pest control in many agricultural areas. These pesticides originate from different sources especially from agricultural drainage [2]; wastewater treatment plants [3] and other water resources. These pesticides are mainly nonbiodegradable environmental pollution and are carcinogenic in nature. Therefore, pesticides toxicity and their post-degradation products that make serious contribution to increased levels of environmental and water contamination have become predominant all around the world [4].

Diazinon is considered as a kind of organophosphate pesticide. Diazinon is utilized as a control measure for pests in fruits, vegetables, and field crops, but excessive concentration of this insecticide has detrimental effect on organisms and blood. Hence, the amount of usage should be carefully determined in case the toxicant contaminates ground or sea water [5,6]. At the same time, diazinon is easily absorbed into the skin and holds a synergic characteristic with other toxins such as pyrethrins [7]. A maximum allowed concentration of 0.5 µg/L was determined by the European Union for the combination of all pesticides and 0.1 µg/L for individual compounds in drinking water [8]. Several techniques were employed to remove the toxicant from water, such as treatment by adsorption processes [9,10], advanced oxidation processes [11,12] and electrocoagulation process [6].

Adsorption reveals one of the most effective methods for the removal of pollutants from the environment. This technique uses an equipment that is easy to use and readily available, yet not energy intensive. The treatment is also cost effective [13-17]. Various adsorbents were utilized for the elimination of diazinon from the water and wastewater such as agricultural soil [18], surfactant modified agricultural soil [19], organo-zeolites [20] and modified bentonite [21].

Perlite is a glassy volcanic rock and its structure is made of more than 70% of silica and 13% of alumina existing in many types and forms. The amounts of silica and alumina vary from type to type [22]. Zeolites were successfully utilized in the chemical industry and environmental protection over the last 35 years in accordance with their significant physical and chemical properties which include molecular sieving, adsorbing and cation exchange capability [23]. Preparation of zeolites from low-cost sources has

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Abbreviations

A	cross sectional area of the adsorber (m^2)
b_i	Langmuir constant (min^{-1})
C_{bi}	concentration of solute i in the fluid phase of the column (kg/m^3)
c_{bi}	scaled concentration of solute i in the fluid phase of the column C_{bi}/C_{oi}
C_e	equilibrium concentration (mg/L)
C_{0i}	initial concentration of solute i (mg/L)
C_{pi}	concentration of solute i in the fluid phase within the pores of the zeolite (kg/m^3)
c_{pi}	scaled concentration of solute i in the fluid phase within the pores of the zeolite C_{pi}/C_{oi}
D_{pi}	pore diffusion coefficient of component i (m^2/s)
$D_{D,j}$	dispersion coefficient of bed (m^2/s)
$D_{e,j}$	dispersion coefficient of bed (m^2/s)
d_p	particle diameter (m)
K_{qt}	life factor in Eq. (30) (mg/g cycle)
K_{tb}	life factor in Eq. (31) (h/cycle)
k_{fi}	external mass transfer coefficient of solute i (m/s)
L	bed height (m)
Q	flow rate (L/s)
q_e	equilibrium zeolite capacity (mg/g)
q_{mi}	adsorption equilibrium constant defined by Langmuir equation of component i (mg/g)
q_T	zeolite capacity in packed bed (mg/g)
q_{TI}	initial zeolite capacity (mg/g)
R	radial distance in the particle (m)
Re	Reynolds number ($\rho \upsilon d_p/\mu_w$)
R_p	radius of particle (m)
r	scaled radial distance in the particle R/R_p
t	time (s)
t_e	breakthrough time (s)
t_b	initial breakthrough time (s)
V_o	initial solution volume (L)
V_f	final solution volume (L)
W_A	zeolite dosage (g)
R_i	reaction rate
S_i	saturation volume

Greek symbols

ε_b	bed porosity
ε_p	particle porosity
υ	interstitial velocity ($Q/A\varepsilon p$) (m/s)
ρ_p	density of particle (kg/m^3)
ρ_w	density of water (kg/m^3)
μ_w	viscosity of water (Pa s)
τ_{fj}	tortuosity coefficient

Subscripts

j	integer value
L	liquid phase
p	pore phase

been the main objective in many researches [24]. Many research groups were formed to prepare zeolites from perlite in laboratories that led to the formation of different types of zeolites, such as zeolite-X, gismondine, heulandite, ZSM-5, *etc.* [25]. A natural zeolite (bentonite) was used in Ouznadji et al. [21] for the sorption of diazinon from aqueous solutions. The latter objective was to explain the effects of different parameters such as pH, temperature, contact time, adsorbent dosage, and initial pesticide concentration on the diazinon removal. In another study, the possibility of using MCM-41 and MCM-48 mesoporous silicas was examined for the diazinon and fenitothion removal from non-polar solvent via the batch sorption method [26]. The organ-zeolite was also employed as a low cost sorbent for the removal of atrazine, lindane and diazinon from water. In addition, the effect of different operating variables was studied on the sorption of atrazine, lindane and diazinon onto organo-zeolite and equilibrium isotherm of this sorption process [20].

The computational fluid dynamics (CFD) method is a useful tool for industrial design and for the validation of experimental data. The main advantage of computational modeling may be that different physical domains can be coupled, and solved efficiently. In fixed beds column, in general, several modes of transport and processes take place simultaneously. For instance, fluid flow, permeation, convection, diffusion and the chemical reactions involved in adsorption. The CFD simulations can be applied by manually written codes or commercial software packages. Some commercial packages, such as COMSOL Multiphysics (Femlab, formerly COMSOL, Inc., Sweden), Fluent (ANSYS, Inc., USA), CFD-ACE+(CFD Research Corp., USA), have become popular in the fluidics community in last decades, since commercial packages are designed to be user friendly [27,28]. The purpose of these programs is to allow researchers who may not be well versed in fluid dynamics to model successfully the channel-fluidic phenomena in an interdisciplinary field such as column adsorption [27,28].

The main objective in this research was to examine the synthesized sodalite zeolite obtained from perlite. Sodalite zeolite was modified by copper oxide (Cu_2O) nanoparticles and utilized as an attractive adsorbent for the diazinon pesticide treatment from aqueous solution. Moreover, the effect of different parameters such as flow rate, initial concentration and bed depth was studied on the removal of diazinon in the column mode. The experimental results were studied thoroughly with the theoretical values which were obtained from the solution of the mathematical model using COMSOL multiphysics software.

2. Experimental work and procedure

2.1. Synthesis of sodalite zeolite

A starting material such as raw perlite was employed with a grain size of <75 µm (72.68 wt.% SiO_2; 11.74 wt.% Al_2O_3). First, the aluminate solution was prepared after 0.873 g Al-foil added to 15 mL of 2.7 N NaOH solution was dissolved. Then, the silicate solution was prepared by mixing 3.651 g of perlite which was later transferred to a polypropylene bottle containing 31 mL of 2.7 N NaOH solution. Through magnetic stirring, the mixture was heated for 2 h. Then, the suspension was filtered.

Next, the silica source was added slowly to the alumina source. The resulting mixture was stirred for 60 min to obtain a homogenous and clear solution. Afterward, the mixture was transferred into a stainless steel autoclave with teflon tube and heated in an oven at 110 °C for 25 h. After the finalization of the hydrothermal treatment, the products were collected by means of filtration, washed with deionized water and dried at 80 °C overnight.

2.2. Synthesis of Cu modified sodalite

Through the grains draining in a dispersed suspension of nanoparticles, nanoparticles coating on zeolite grains was carried out. Typically, 0.1 g copper oxide (Cu_2O) with a particle size of 30–60 nm was spilled into an Erlenmeyer flask containing 10 mL distilled water and later sonicated for a few minutes to make a uniform suspension. Then, 2 g sodalite zeolite was added to the flasks and shook moderately for 2 h. Ultimately, the flasks contents were dried slowly at 80 °C for 10 h. The added value of nanoparticles was 4.5 wt.% of zeolite [29,30].