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A study on the kinetics of 2-chloroethyl ethyl sulfide adsorption onto nanocomposite activated carbon nanofibers containing metal oxide nanoparticles

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ABSTRACT

This paper discusses the adsorption kinetics, namely the rate constant and the half-life of 2-chloroethyl ethyl sulfide (2-CEES) onto activated carbon nanofibers (ACNFs) embedded with MgO and Al_2O_3 nanoparticles. ACNFs especially when embedded with catalytic metal oxides like MgO and Al_2O_3 are a very good candidate for decontaminating harmful chemicals. The results of this research shows that the pseudo-second order model predicts the adsorption kinetics of 2-CEES onto composite ACNFs embedded with MgO and Al_2O_3 nanoparticles. It was also found that increasing the amount of MgO and Al_2O_3 nanoparticles of both regular and Plus grades, increases the rate constant of the 2-CEES adsorption onto ACNFs. Moreover, the Plus grade of MgO and Al_2O_3 nanoparticles show higher rate constants and lower half-lives, thanks to their higher specific surface area. However, normal grade of Al_2O_3 nanoparticles show a higher rate constant than normal grade of MgO nanoparticles.

1. Introduction

The carbonaceous adsorbents such as activated carbons, especially the nanofibrous and regular fibrous types, have attracted a considerable deal of attention in decontamination of harmful chemicals [1–8]. Activated carbon nanofibers (ACNFs) adsorb toxic liquids and gases and hold them physically [9,10]. ACNFs embedded with metal oxides like MgO or Al_2O_3, have the advantage of being able to destruct the adsorbed gases or liquids, thanks to their catalytic behavior [4,11–13], which makes them effective in applications like destructive filtration and protective clothing [14]. Apart from the adsorption capacity, the adsorption rate is also important in filtration and protective systems. It is worth mentioning that the adsorption rate of adsorbing media, i.e. protective clothings, depends on the specific surface area as well as the pore characteristics of the fibers forming the adsorbent. Total pore volume, micropore volume, mesopore volume, and pore size distribution constitute the main characteristics of porous structures [12,15].

Adsorption kinetics which give information about the rates at which the adsorbates are adsorbed onto the adsorbents [16] has been studied mostly under static conditions for ACNFs as adsorbent where the adsorbate diffuses into micropores of ACNFs with a size less than 2 nm [14,17]. Adsorption of toxic liquids and gases under static conditions makes the adsorbate hold to the adsorbent for a considerably longer time, when compared with the adsorption under dynamic conditions [17]. Amongst the several mathematical models which have been produced to describe the adsorption kinetics of toxic liquids and gases onto ACNFs, the pseudo-first order and pseudo-second order equations, as shown in Eqs. (1) and (2), respectively, are the most promising ones [18].

$$\ln([A]_0 - [A]_t) = \ln[A]_0 - k_1 t \quad (1)$$

$$1/[A]_t = k_2 t + 1/[A]_0 \quad (2)$$

where $[A]_0$ and $[A]_t$ are the initial and at time (t) concentration of adsorbate, respectively and k_1 and k_2 show the rate constant of pseudo-first order and pseudo-second order adsorptions, respectively. As can be seen, in a pseudo-first order reaction, the rate is linearly proportional to the concentration of one of the reactants; whereas in pseudo-second order reaction, the rate is proportional to the square of the concentration of a single adsorbate [19].

Adsorption rate constant (k) and adsorption half-life constitute the two basic factors which describe the characteristics of adsorption kinetics. Rate constant can be designated with a minus or plus sign, depending on whether the adsorbate is a reactant or a reaction product, respectively. Half-life shows the time needed for concentration to fall to half of its initial value [20,21]. The higher the rate constant and the lower the half-life, the faster is the adsorption. The half-life of pseudo-first order and pseudo-second order adsorptions are shown in Eqs. (3) and (4), respectively.

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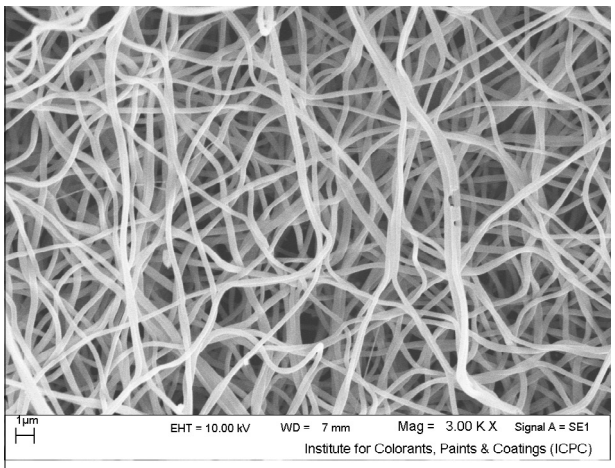

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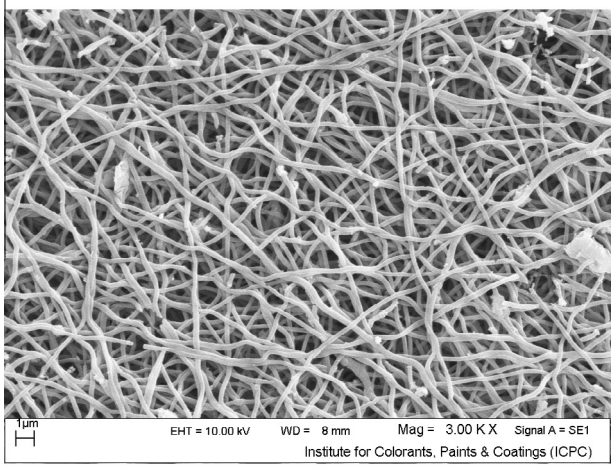

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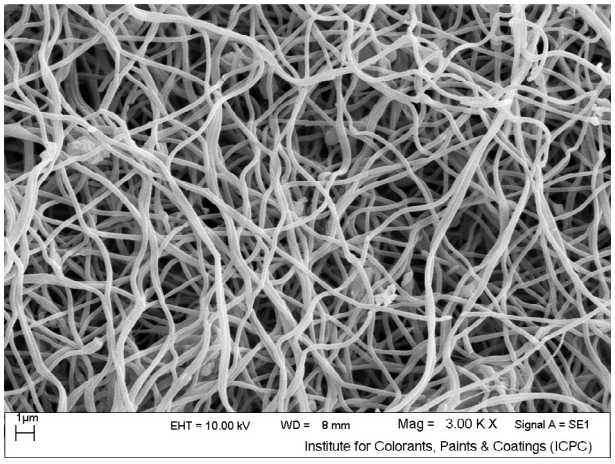

(c)

Fig. 1. SEM images of ACNFs embedded with: (a) no metal oxide nanoparticles, (b) 10 wt.% MgO Plus, and (c) 10 wt.% Al_2O_3 Plus nanoparticles.

$$\text{Half-life (pseudo-first order)} = (\ln 2)/k_1 \quad (3)$$

$$\text{Half-life (pseudo-second order)} = 1/k_2[A]_0 \quad (4)$$

A brief literature review concerning the adsorption kinetics involving 2-chloroethyl ethyl sulfide (2-CEES) and ACNFs follows next. It is worth mentioning that 2-CEES is a mustard agent surrogate.

Saxena et al. [22] obtained the kinetics parameters of 2-CEES adsorption onto Al_2O_3 nanoparticles under static conditions. Saxena et al. [17] also obtained the adsorption kinetics parameters of 2-CEES and bis-2-chloroethyl sulfide on silica nanoparticles under static conditions and related the high destructive adsorption capacity of silica nanoparticles to the diffusion of 2-CEES molecules onto the reactive sites of nanoparticles. In another work, Saxena et al. [14] investigated the adsorption kinetics of dimethyl methyl phosphonate gas onto metal impregnated granular activated carbon under static conditions. Karwacki et al. [23] studied the adsorption kinetics of isopropyl methyl phosphonofluoridate onto granular activated carbon at ultra low relative pressure. Karwacki et al. [24] also investigated the influence of temperature on the adsorption kinetics of bis-2-chloroethyl sulfide onto granular activated carbon with and without co-adsorbed water. Lee et al. [8] compared the formaldehyde adsorption capacity of ACNFs with the regular fibrous type and showed the superiority of ACNFs in the humid conditions. Park et al. [25] studied the adsorption kinetics of acetaldehyde onto functionalized corn-based activated carbon and found that the pseudo-second order equation was a much better means of describing the adsorption kinetics. Shim et al. [26] evaluated the adsorption kinetics of benzene onto ACNFs and found that benzene could be effectively adsorbed by micropores as well as a small amount of the mesopores of ACNFs. Moreover, it has also been revealed that the adsorption kinetics of some heavy metallic ions in aqueous solutions on granular activated carbon, predominantly follows the pseudo-second order equation [27–29]. Cai et al. [30,31] have shown that a combination of several factors, such as phase structure, specific surface area, pore volume, and the unique morphology can be held responsible for the discrepancies concerned with the removal of organic pollutants by boehmite which is a kind of alumina hydrate.

Considering the very good potentials of ACNFs as harmful chemical adsorbing protective clothings [9,32,33], this study aimed at investigating the effect of the amount and specific surface area of MgO and Al_2O_3 nanoparticles on the adsorption kinetics namely, the rate constant and the half-life of 2-CEES onto ACNFs embedded with them.

2. Experimental

2.1. Materials

Metal oxide nanoparticles, namely MgO (crystalline, crystal size $\leqslant$ 8 nm, specific surface area = 230 m^2/g), MgO Plus (crystalline, crystal size $\leqslant$ 4 nm, specific surface area = 600 m^2/g), Al_2O_3 (amorphous, specific surface area = 275 m^2/g), and Al_2O_3 Plus (amorphous, specific surface area = 550 m^2/g) were purchased from Nanoscale, USA. Polyacrylonitrile (PAN) powder was provided by Iran Polyacryl Company. Dimethylformamide (DMF) and cyclohexane as solvent and xylene as internal standard were purchased from Merck, Germany. 2-CEES was purchased from Sigma–Aldrich, USA. All reagents were used as received.

2.2. Fabrication of metal oxide free and composite PAN nanofibrous precursor

To electrospin the PAN nanofibrous precursor, solutions consisting of 5, 10, and 15 wt.% MgO and 10, 15, and 20 wt.% Al_2O_3 nanoparticles (relative to PAN weight) were prepared. The metal oxides were added to DMF first and then mixed by magnetic stirrer for 1 h at ambient temperature. PAN powder (18 wt.% relative to DMF weight) was then dissolved in DMF containing the nanoparticles. This was followed by stirring for 20 h at ambient temperature. Finally, in order to ascertain an optimum dispersion of nanoparticles