Removal of humic acid from aqueous solution using dual PMMA/PVDF composite nanofiber: kinetics study

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Abstract. The removal of humic acid from aqueous solution using dual poly(methyl methacrylate)/polyvinyl difluoride composite nanofiber under the influence of concentration has been studied. The experiments were performed using humic acid (HA) as an adsorbate at concentration in the range of 50-200 mg/L. Pseudo-first-order, pseudo-second-order, and intra-particle diffusion models were used to describe the kinetic data and the rate constants were evaluated. It was observed that the amount of humic acid removed decrease with increasing concentration. The kinetic study revealed that pseudo-second order model fitted well the kinetic data, while the external diffusion or boundary layer diffusion was the main rate determining step in the removal process.

1. Introduction
Humic acid (HA) is a subclass of humic substances and accounts for a significant portion (40-90%) of the dissolved organic matter found in nearly all water supplies. The chemical and physical characteristics of humic acid, which have not been precisely defined, are strongly dependent on the source they originate [1], and consisted of large molecules with molecular weights ranging from thousands to hundreds of thousands [1-3]. HA molecule contains functional groups such as carboxylic, phenolic, carbonyl, hydroxyl, aldehyde acid, and methoxyl. The existence of carboxylic and phenolic groups results in predominantly carrying negative charges in aqueous solutions [1]. Humic acid imparts a brown or yellow color in peat water and pose a serious environmental problem, particularly in drinking water treatment because of their taste and odor [1,3,4]. HA also may cause a serious problem for drinking water production because HA can form carcinogenic disinfection by-products (DBPs) such as trihalomethanes (THMs) during chlorination process [1-8]. In addition, HA could enhance the transport of some persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) to aquatic organisms [9,10]. Therefore, it is of great importance to remove HA from water and wastewater in terms of protecting human health and environment.

Conventional treatment processes include the coagulation and flocculation [4,6,8], oxidation [6], photocatalysis [7], biofiltration [9] and membrane filtration [4], techniques have been developed to remove these substances. All of these alternative processes, however, have disadvantageous, e.g: high
operational cost and requires some chemicals. None of them therefore, is considered by industries to be commercially viable because economically unrealistic.

Due to its easy to operate and most effective, adsorption has been considered as one of the most economically promising techniques for the water and wastewater treatments [11]. Most conventional adsorption plants use activated carbon, because of its extended surface area, microporous structure, high adsorption capacity and high degree of surface reactivity [12,13]. However, the major drawback of activated carbon is the high operating cost.

Now day, polymeric adsorbents have been increasingly used to remove and recover organic pollutants from wastewater due to their high specific area and high adsorption capacity. The materials can be made into nanofiber by electrospinning, which make it easy for regeneration [3]. In this work, effects of initial HA concentration on the removal ability of dual PMMA/PVDF composite nanofiber as an adsorbent from aqueous solutions was examined. Pseudo first, second order and intra-particles adsorption kinetics were applied to the experimental results and kinetic parameters were also calculated.

2. Methods

2.1. Materials
Dual PMMA/PVDF composite nanofiber was obtained from Analytical Chemistry Laboratory, Institut Teknologi Bandung. Water used was generated from aqua demineralization system. The humic acid sample was obtained from Merck. Before mixing the humic acid sample with adsorbent, its pH value was adjusted using sodium hydroxide or hydrochloric acid. The pH value was measured using 300 Hanna Instrument pH meter.

2.2. Method
Adsorption experiments were carried out in 100 mL flasks containing 50 mL of HA solution with various initial concentrations (50-200 mg/L) and 0.05 g adsorbent. These mixtures immersed in a thermostatic shaker bath at 25 °C in thermostatic shaker bath for 2, 5, 10, 15, 20, 30, 40, 60, 80, 100, 120 and 180 minutes. At the end of the predetermined time interval, the mixtures were taken out and the supernatant was centrifuged at 300 rpm for 10 minutes. The HA concentration was determined by spectrophotometer (Shimadzu UV-Vis, 1601 model) at the λ 300 nm. The percent removal of HA was calculated using the following equation:

\[
\% \text{ Removal} = \frac{C_i - C_e}{C_i} \times 100
\]

where \(C_i\) and \(C_e\) are initial and final concentration (mg/L) of HA in solution, respectively. The adsorption capacity of an adsorbent at equilibrium with solution volume \(V\), was calculated using the following equation:

\[
q_e \text{ (mg/g)} = \frac{C_i - C_e}{m} \times V
\]

where \(C_i\) and \(C_e\) are the initial and final concentration (mg/L) of HA in solution, respectively.

3. Results and Discussion
The removal of HA using dual PMMA/PVDF composite nanofiber as a function of contact time at various initial concentrations is shown in Figure 1. The rate of HA removal using dual PMMA/PVDF nanofiber was studied using initial HA concentrations ranging from 50 to 200 mg/L. Results showed that the rate of removal was rapid at the beginning and gradually decreased with increasing contact time until equilibrium was attained. Based on these plots, the equilibrium has been established at 60 minutes.
Figure 1. Effect of concentration on HA removal using dual PMMA/PVDF composite nanofiber

From Figure 1, we can also observe that the initial HA concentration had a significant effect on HA removal. The percentage of HA removal at equilibrium decreased as the HA concentration was increased. This is because an increase in the initial concentration provides an important driving force to overcome all resistances of the HA molecules between the aqueous and solid phases [1,3,13-15]. At lower concentrations, all sorbate ions present in the sorption medium could interact with the binding sites, hence higher percentage adsorption results. At higher concentrations, because of the saturation of the sorption sites, the percentage adsorption of the HA molecules shows a decreasing trend [3,13,15].

The models of adsorption kinetics were correlated with the solution uptake rate, hence these models are important in water treatment process design [16,17]. In order to elucidate the adsorption mechanism and adsorption rate controlling step, three kinetic models: the pseudo-first-order equation, the pseudo second-order equation, and intra-particle diffusion equation are tested to fit experimental data obtained from batch experiments.

The linearized form of pseudo-first-order kinetic model is given as follows:

\[
\log(q_e - q_t) = \log q_e - (k_1/2.303) t
\]

where \( k_1 \) is the adsorption rate constant (1/min), \( q_e \) and \( q_t \) are the amounts of HA adsorbed at equilibrium and at time \( t \) (min). The linear plot of \( \log(q_e - q_t) \) versus \( t \) was used to calculate the rate constant \( k_1 \), the equilibrium adsorption capacity \( q_e \), and the determination coefficient \( R^2 \), and the results are given in Table 1. Although the \( R^2 \) value obtained was relatively high, the calculated \( q_e \) value did not agree with the experimental one. This suggests that the pseudo-first-order kinetic model is not appropriate to represent the removal kinetics data of HA using dual PMMA/PVDF composite nanofiber.

### Table 1. Pseudo-first and pseudo-second order kinetics parameters for HA removal.

| \( C_0 \) (mg/L) | \( q_{exp} \) (mg/g) | \( k_1 \) (1/min) | \( q_{cal} \) (mg/g) | \( R^2 \) | \( k_2 \) (g/mg.min) | \( q_{cal} \) (mg/g) | \( R^2 \) |
|-----------------|-------------------|-----------------|-------------------|------|-----------------|-------------------|------|
| 50              | 0.991             | 0.099           | 0.980             | 0.993| 0.128           | 0.092             | 0.999|
| 100             | 1.243             | 0.081           | 1.529             | 0.965| 0.092           | 1.246             | 0.998|
| 150             | 1.835             | 0.057           | 2.099             | 0.972| 0.076           | 1.822             | 0.999|
| 200             | 2.247             | 0.043           | 2.536             | 0.976| 0.049           | 2.251             | 0.998|

The kinetic data were further analyzed using pseudo-second-order kinetic model. This model is based on the assumption of chemisorption of the adsorbate on the adsorbents. This model is given as:

\[
\frac{t}{q_t} = \frac{1}{k_2 q_e^2 + t/q_e}
\]
where \( k_2 \) (g/(mg min\(^{-1}\))) is the rate constant of pseudo-second-order adsorption. The values of equilibrium adsorption capacity \( q_e \) and rate constant \( k_2 \), calculated from the intercept and the slope of the linear plot of \( t/q_t \) versus \( t \), along with the value of determination coefficient \( R^2 \), are listed in Table 1.

The linear plots of \( t/q_t \) versus \( t \) show a good agreement with experimental data giving the correlation coefficients close to 1. Also, the calculated \( q_e \) values agree very well with the experimental data at all initial HA concentrations. This means that the adsorption system obeys the pseudo-second-order kinetic model for the entire removal period.

The pseudo-second-order kinetic model cannot give a definite mechanism of adsorption (or removal). Adsorption kinetics is usually controlled by different mechanisms, the most general of which is the diffusion mechanism. To investigate the mechanism of adsorption, the intra-particle diffusion model is used. The intra-particle diffusion model can be defined as:

\[
q_t = k \cdot t^{1/2} + C
\]

where \( k \) and \( C \) are an intra-particle diffusion rate constant (mg/g.min\(^{1/2}\)) and a constant, respectively. The plot of \( q_t \) versus \( t^{1/2} \) would result in a linear relationship. If the lines passed through the origin, only diffusion would be the controlling step. Otherwise, the intra-particle diffusion is involved in the sorption process but is not the only rate-controlling step [1,13,14].

The sorption rate is known to be controlled by several factors including (i) diffusion of the solute from the solution to the film surrounding the particle, (ii) diffusion from the film to the particle surface (external diffusion), (iii) diffusion from the surface to the internal sites (surface diffusion or pore diffusion) and (iv) uptake which can involve several mechanisms such as physico-chemical sorption, ion exchange, precipitation or complexation [13,18,19]. Adsorption kinetics are usually controlled by different mechanisms, of which the most limiting ones are the diffusion mechanisms, including the initial curved portion, which is attributed to rapid external diffusion or boundary layer diffusion and surface adsorption, and the linear portion, i.e. a gradual adsorption stage due to intra-particle diffusion, followed by a plateau to equilibrium where the intra-particle diffusion starts to decrease due to the low concentration in solution as well as fewer available adsorption sites [13,20].

In the case of removal of HA using dual PMMA/PVDF composite nanofiber the plots present a multi-linearity indicating that two steps are taking place (Figure not shown). The general features of the plots are an initial linear portion (0-15 min) and a plateau (after 15 min). The first linear region is related to the instantaneous adsorption stage \( (k_{d1}) \) that represents boundary layer diffusion effects. The second linear \( (k_{d2}) \) is a relatively slow adsorption region. This stage is a result of intra-particle diffusion effects [13-15,21], which is the rate-limiting step.

### Table 2. Parameters of the intra-particle diffusion model for HA removal.

| \( C_0 \) (mg/L) | \( k_{d1} \) (mg/g.min\(^{1/2}\)) | \( C_1 \) | \( R_1^2 \) | \( k_{d2} \) (mg/g.min\(^{1/2}\)) | \( C_2 \) | \( R_2^2 \) |
|------------------|-------------------|--------|--------|-------------------|--------|--------|
| 50               | 0.640             | -0.078 | 0.988  | -0.007            | 3.568  | 0.604  |
| 100              | 0.713             | 0.122  | 0.988  | 0.004             | 3.722  | 0.317  |
| 150              | 0.858             | 0.253  | 0.981  | -                 | 3.871  | -      |
| 200              | 0.876             | 0.361  | 0.980  | 0.008             | 3.882  | 0.521  |

Extrapolating the linear portion of the plot yields the intercept \( (C) \) is proportional to the extent of boundary layer thickness [13-15]. The values of constants \( k_{d1} \) and \( k_{d2} \) for intra-particle diffusion kinetics have been derived from the slopes of the linear portions and are represented in Table 2. The results indicate that the external diffusion or boundary layer diffusion model fits the experimental data very well for an initial period of 15 min of the removal process.
4. Conclusion
The main aim of this study was to investigate the adsorption kinetics of HA removal using dual PMMA/PVDF composite nanofiber as an adsorbent. The results from this work showed that the HA initial concentration has an important role in the removal of HA using dual PMMA/PVDF composite nanofiber. The removed amounts of HA increased with increase in contact time and reached equilibrium within 60 minutes. The equilibrium time is independent of initial HA solution concentration. The kinetic of removal was studied by using pseudo-first and pseudo-second-order kinetic models and the intra-particle diffusion equation. With respect to the suitability of pseudo-first and pseudo-second-order kinetic models for HA removal using dual PMMA/PVDF composite nanofiber, it has been represented that for the examined system the pseudo-second-order kinetic provided the best correlation of the experimental data, with a rate constant in the range of 0.049-0.128 g.mg⁻¹.min⁻¹. The results from assessing intra-particle diffusion model revealed that intra-particle diffusion is not the only process controlling the HA removal using dual PMMA/PVDF composite nanofiber.

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