

## **Adsorption of Humic Acid from Aqueous Solution onto PMMA Nanofiber: Kinetics Study**

Muhammad Ali Zulfikar <sup>1+</sup>, Afdal Bahri <sup>1</sup> and Muhammad Nasir <sup>2</sup>

<sup>1</sup> Analytical Chemistry Research Group, Institut Teknologi Bandung  
Jl. Ganesa 10 Bandung 40132, Indonesia

<sup>2</sup> Institute of Indonesian Science, Jl. Cisit 2, Bandung 40132, Indonesia

**Abstract.** The effect of concentration on humic acid (HA) adsorption using PMMA nanofiber has been studied. The experimental data were analyzed by pseudo-first-kinetic, pseudo-second-kinetic and particle diffusion models. From experiment it can be seen that the HA adsorption using PMMA nanofiber decreased with increasing its concentration. The adsorption kinetic data of HA on PMMA nanofiber was well described by a pseudo-second-order model, with the kinetic constants in the range of 0.039 - 0.079 g mg<sup>-1</sup> min<sup>-1</sup>. Concerning the mechanism, the results indicated that the intra-particle diffusion is not the rate limiting step in the HA adsorption process.

**Keywords:** adsorption, humic acid, kinetics, nanofiber

### **1. Introduction**

Humic acid (HA) is a component of natural organic matter (NOM) in surface and ground water, which is derived from the breakdown of plant biomass [1], [2]. HA 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], [2]. In addition, HA could enhance the transport of some persistent organic pollutants such as polycyclic aromatic hydrocarbons (PAHs) to aquatic organisms [3], [4]. Therefore, it is of great importance to remove HA from water and wastewater in terms of protecting human health and environment.

There are various technologies to remove HA from water and wastewater, such as chemical oxidation, electrochemical process, coagulation, ultrafiltration, biological process and membrane technology [5]-[10]. Due to it's 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.

Some mesoporous organic/inorganic composite nanomaterials are potential adsorbents for pollutants removal from the aqueous phase due to their high specific surface area. The materials can be made into nanofiber membranes by electrospinning, which make it easy for regeneration. In the present study, effects of initial HA concentration on the removal ability of PMMA nanofiber as an adsorbent from aqueous solutions was examined. Both pseudo first and second order adsorption kinetics were applied to the experimental results and kinetic parameters were also calculated.

---

<sup>+</sup> Corresponding author. Tel.: +62222502103; fax: +62222504154  
*E-mail address:* zulfikar@chem.itb.ac.id

## 2. Methodology

### 2.1. Materials

PMMA nanofiber was obtained from Center for Chemistry Research, Indonesian Institut of Science, Bandung, Indonesia. Humic acid (HA) was purchased from Merck. Hydrochloric acid used to adjust pH was purchased from Merck. Water used was generated from aqua demineralization system. All materials were used without further purification. Before mixing the HA sample with adsorbent, its pH value was adjusted and measured using 300 Hanna Instrument pH meter.

### 2.2. Methods

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 suspension was taken out and the supernatant was centrifugated at 300 rpm for 10 minutes. The HA concentration was determined by spectrophotometer (Shimadzu UV-Vis 1601 model) at the  $\lambda$  300 nm. The percent of HA adsorption was calculated using the following equation:

$$\text{Adsorption (\%)} = [(C_i - C_e)/C_i] \times 100\% \quad (1)$$

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:

$$q_e (\text{mg}\cdot\text{g}^{-1}) = [(C_i - C_e)/m] \times V \quad (2)$$

where  $C_i$  and  $C_e$  are the initial and final concentration (mg/L) of HA in solution, respectively.  $V$  is the volume of solution (L) and  $m$  is mass of adsorbent (g) used.

## 3. Results and Discussion

The adsorption of HA onto PMMA nanofiber as a function of contact time at various initial concentrations is shown in Fig. 1. Results showed that the rate of adsorption was rapid at the beginning and gradually decreased with increasing contact time until equilibrium was attained.

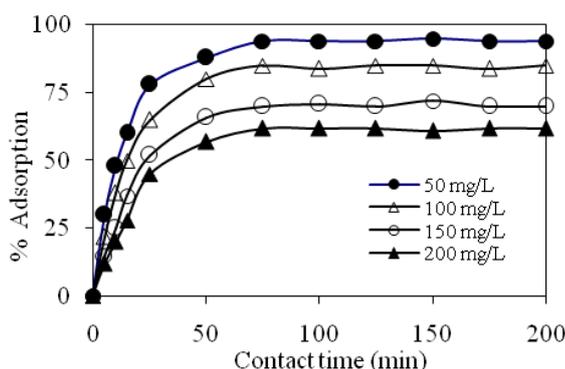


Fig. 1: Effect of concentration on HA adsorption onto PMMA nanofiber

As shown in Fig. 1, the initial dye concentration had a significant effect on HA adsorption. The percentage of HA adsorption 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 dye between the aqueous and solid phases [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 dye shows a decreasing trend [13], [15].

Adsorption kinetics is an important parameter for designing adsorption systems and is required for selecting optimum operating conditions for batch adsorption study. To investigate the adsorption kinetics of HA adsorption onto PMMA nanofiber, two widely used kinetic models, pseudo-first-order and pseudo-second-order kinetic models, were employed to interpret the kinetics results. The linearized form of pseudo-first-order kinetic model is given as follows:

$$\log (q_e - q_t) = \log q_e - (k_1/2.303) t \quad (3)$$

where  $q_e$  and  $q_t$  are the amounts of HA adsorbed (mg/g) at equilibrium and at time ( $t$ ), respectively, and  $k_1$  ( $\text{min}^{-1}$ ) is the rate constant of this equation. 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 I. Although the  $R^2$  value obtained was relatively high ( $R^2 = 0.985$ ), 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 adsorption kinetics data of HA onto PMMA nanofiber.

Table I: Pseudo-first and pseudo second order kinetics parameters for HA adsorption

$C_o$ (mg/L)	$q_{e, \text{exp}}$ (mg/g)	Pseudo-first-order model			Pseudo-second-order model		
		$k_1$ (1/min)	$q_{e, \text{cal}}$ (mg/g)	$R^2$	$k_2$ (g/mg.min)	$q_{e, \text{cal}}$ (mg/g)	$R^2$
50	0.988	0.079	0.980	0.998	0.134	1.028	0.999
100	1.782	0.047	1.529	0.985	0.049	1.727	0.998
150	2.362	0.045	2.099	0.992	0.027	2.387	0.996
200	2.865	0.039	2.536	0.981	0.017	2.846	0.993

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

$$t/q_t = 1/k_2 \cdot q_e^{-2} + t/q_e \quad (4)$$

where  $q_e$  and  $q_t$  are the amounts of HA adsorbed (mg/g) on adsorbents at equilibrium, and at time  $t$ , respectively and  $k_2$  is the rate constant ( $\text{g/mg} \cdot \text{min}^{-1}$ ). 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 I. The correlation coefficients for the pseudo-second-order kinetic model value obtained was very high ( $R^2 > 0.999$ ), and the calculated  $q_e$  value was in good agreement with the experimental one. These indicate that the adsorption system belongs to the pseudo-second-order kinetic model.

Table I, it also show that the values of the rate constant  $k_2$  decrease with increasing initial concentrations. The reason for this behavior can be attributed to the decrease in the mobility of its molecule with increasing initial concentration which may be due to these molecules to aggregate at higher concentration and consequently lower diffusion rates are obtained.

The evaluation of the diffusion mechanism is not possible from the pseudo first order and second order kinetic models. Therefore, to analyze the mechanism of removal process, the intra-particle diffusion model can be used. 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 [16], [17]. The overall rate of the sorption process will be controlled by the slowest step, i.e. the rate limiting step. This model showed that the sorption process is diffusion controlled if

the rate is dependent upon the rate at which adsorbate and adsorbent diffuse towards one another. Intra-particle diffusion was characterized using the relationship by [18]-[20]:

$$q_t = k.t^{0.5} + c \quad (5)$$

where  $k$  and  $c$  are an intra-particle diffusion rate constant ( $\text{mg/g.min}^{0.5}$ ) and a constant, respectively. The  $k$  is obtained from the slope of linear plot of  $q_t$  vs.  $t^{0.5}$ . From plot of  $q_t$  against  $t^{0.5}$  (Figure not shown here) it can be seen that these plots generally have a dual nature, i.e., an initial curved portion and a final linear portion may be explained by the fact that the initial curved portion represents boundary layer diffusion effects. The final linear portions are a result of intra-particle diffusion effects [19]. Extrapolating the linear portion of the plot to the ordinate produces the intercept ( $c$ ) which is proportional to the extent of boundary layer thickness [18].

Referring to intra-particle diffusion plot, the first stage was completed within the first 15 min and the second stage of intra-particle diffusion control was then attained. The plot also showed that the linear lines of the second stages did not pass through the origin and this deviation from the origin or near saturation might be due to the difference in the mass transfer rate in the initial and final stages of adsorption [21]. It confirms that intra-particle diffusion was not the only rate limiting mechanism in the removal process [22].

Table II: Intra-particle diffusion kinetic model parameters for HA adsorption

$C_o$ (mg/L)	$k_{d1}$ ( $\text{mg/g.h}^{0.5}$ )	$C_1$	$R_1^2$	$k_{d2}$ ( $\text{mg/g.h}^{0.5}$ )	$C_2$	$R_2^2$
50	0.342	0.375	0.995	0.032	4.125	0.918
100	0.425	0.422	0.989	0.052	7.222	0.898
150	0.854	0.846	0.982	0.072	8.450	0.886
200	1.772	2.224	0.946	0.091	9.555	0.869

The values of  $k_{d1}$  and  $k_{d2}$  as obtained from the slopes of the two straight lines are listed in Table II. In order to determine the thickness of the boundary layers due to both the film diffusion and the intra-particle diffusion, the values of  $C_1$  and  $C_2$  are tabulated in Table II. The thickness of the boundary layer in the second portion that corresponds to the intra-particle diffusion ( $C_2$ ) is larger than that of the first portion that concerned the film diffusion ( $C_1$ ). Consequently the values of the intra-particle diffusion rates  $k_{d2}$  are smaller than the film diffusion rates  $k_{d1}$  [20]. That gives prediction that the humic acid removal process may be controlled by the intra-particle diffusion [20], [23].

## 4. Conclusion

The main aim of this study was to investigate the adsorption kinetics of HA adsorption onto PMMA nanofiber as an adsorbent. The result from this work showed that the HA initial concentration has an important role in the adsorption of HA onto PMMA nanofiber. Kinetic parameters data indicated that the HA sorption process follow pseudo-second-order model, with a rate constant in the range of  $0.039\text{-}0.079 \text{ g.mg}^{-1}.\text{min}^{-1}$ . The results from assessing intra-particle diffusion model revealed that intra-particle diffusion is not the only process controlling the HA adsorption on PMMA nanofiber.

## 5. Acknowledgements

The author is very grateful to Higher Education General for the financial support this research study through Riset Desentralisasi 2016.

## 6. References

- [1] J. H. Wang, S. R. Zheng, J. L. Liu, and Z. Y. Xu. Tannic acid adsorption on aminofunctionalized magnetic mesoporous silica. *Chem. Eng. J.* 2010, **165**: 10-16.
- [2] J. N. Wang, A.M. L. Li., Xu, and Y. Zhou. Adsorption of tannic and gallic acids on a new polymeric adsorbent and the effect of Cu(II) on their removal. *J. Hazard. Mater.* 2009, **169**: 794-800.

- [3] T. L. T. Laak, M. A. T. Bekke, and J. L. M. Hermens. Dissolved organic matter enhances transport of PAHs to aquatic organisms. *Environ. Sci. Technol.* 2009, **43** (19): 7212-7217.
- [4] H. Wang, A. A. Kellerb, and K. K. Clark. Natural organic matter removal by adsorption onto magnetic permanently confined micelle arrays. *J. Hazard. Mater.* 2011, **194**: 156-161.
- [5] J. C. Rojas, J. Pérez, G. Garralón, F. Plaza, B. Moreno, and M. A. Gómez. Humic acids removal by aerated spiral-wound ultrafiltration membrane combined with coagulation–hydraulic flocculation. *Desalination.* 2011, **266**: 128-133.
- [6] C. S. Uygunera, S. A. Suphandaga, A. Kercb, and M. Bekbolet. Evaluation of adsorption and coagulation characteristics of humic acids preceded by alternative advanced oxidation techniques. *Desalination.* 2007, **210**: 183-193.
- [7] C. Sun, Q. Yue, B. Gao, R. Mu, J. Liu, Y. Zhao, Z. Yang, and W. Xu. Effect of pH and shear force on flocs characteristics for humic acid removal using polyferric aluminum chloride organic polymer dual-coagulants. *Desalination.* 2011, **281**: 243-247.
- [8] J. Wang, X. Han, H. Ma, Y. Ji and L. Bi. Adsorptive removal of humic acid from aqueous solution on polyaniline/attapulgitic beads. *Chem. Eng. J.* 2011, **173**: 171-177.
- [9] N. A. A. Hamid,, A. F. Ismail, T. Matsuura, A. W. Zularisam, W. J. Lau, E. Yuliwati, and M. S. Abdullah. Morphological and separation performance study of polysulfone/titanium dioxide (PSF/TiO<sub>2</sub>) ultra filtration membranes for humic acid removal. *Desalination.* 2011, **273**: 85-92.
- [10] K. S. Katsoufidou, D. C. Sioutopoulos, S. G. Yiantsios, and A. J. Karabelas. UF membrane fouling by mixtures of humic acids and sodium alginate: Fouling mechanisms and reversibility. *Desalination.* 2010, **264**: 220-227.
- [11] M. C. S. Reddy, L. Sivaramakrishna and A. V. Reddy. The use of an agricultural waste material, Jujuba seeds for the removal of anionic dye (Congo red) from aqueous medium. *J. Hazard. Mater.* 2012, **203-204**: 118-127.
- [12] P. K. Malik. Use of activated carbon prepared from sawdust and rice husk for adsorption of acid dyes: a case study of acid yellow 36. *Dyes and Pigm.* 2003, **56**: 239-249.
- [13] M. Toor and B. Jin. Adsorption characteristics, isotherm, kinetics, and diffusion of modified natural bentonite for removing diazo dye. *Chem. Eng. J.* 2012, **187**: 79-88.
- [14] M. A. Zulfikar and H. Setiyanto. Adsorption of congo red from aqueous solution using powdered eggshell. *Int. J. ChemTech. Res.* 2013, **5** (4): 1532-1540.
- [15] M. A. Zulfikar, D. Wahyuningrum and S. Lestari. Adsorption of lignosulfonate compound from aqueous solution onto chitosan-silica beads. *Sep. Sci. Technol.* 2013, **48**: 1391-1401.
- [16] O. Gerçel, A. Ozcan, A. S. Ozcan and H. F. Gerçel. Preparation of activated carbon from a renewable bio-plant of *Euphorbia rigida* by H<sub>2</sub>SO<sub>4</sub> activation and its adsorption behavior in aqueous solutions. *Appl. Surf. Sci.* 2007, **253**: 4843-4852.
- [17] F. C. Wu, R. I. Tseng and R. S. Jung. Kinetic modeling of liquid-phase adsorption of reactive dyes and metal ions on chitosan. *Water Res.* 2001, **35**: 613-618.
- [18] C. K. Jain and M. K. Sharma. Adsorption of cadmium on bed sediments of river Hindon: Adsorption models and kinetics. *Water Air Soil Poll.* 2002, **137**: 1-19.
- [19] M. Ugurlu, A. Gurses, M. Yalcin and C. Dogar. Removal of phenolic and lignin compounds from bleached kraft mill effluent by fly ash and sepiolite. *Adsorption.* 2005, **11**: 87-97.
- [20] M. F. Elkady, A. M. Ibrahim and M. M. Abd El-Latif. Assessment of the adsorption kinetics, equilibrium and thermodynamic for the potential removal of reactive red dye using eggshell biocomposite beads. *Desalination.* 2011, **278**: 412-423.
- [21] K. Mohanty, D. Das and M.N. Biswas. Adsorption of phenol from aqueous solutions using activated carbons prepared from *Tectona grandis* sawdust by ZnCl<sub>2</sub> activation. *Chem. Eng. J.* 2005, **115**: 121-131.
- [22] I.A.W. Tan, A.L. Ahmad and B.H. Hameed. Adsorption isotherms, kinetics, thermodynamics and desorption studies of 2,4,6-trichlorophenol on oil palm empty fruit bunch-based activated carbon. *J. Hazard. Mater.* 2009, **164**: 473-482.

[23] M.M. Abd El-Latif and A.M. Ibrahim. Removal of reactive dye from aqueous solutions by adsorption onto activated carbons prepared from oak sawdust. *Des. Water Treat.* 2010, **20**: 102-113.