Adsorption of Humic Acid onto Chitin and Chitosan

W. S. WAN NGAH, A. MUSA

School of Chemical Sciences, Universiti Sains Malaysia, 11800 Penang, Malaysia

ABSTRACT: The adsorption of humic acid onto chitin and chitosan has been investigated. The uptake of humic acid from aqueous solution was determined from changes in concentration, as measured by ultraviolet–visible spectroscopy. The decrease in humic acid removal was observed with the increase in pH. A significant uptake of humic acid on both chitin and chitosan was observed. The uptake of humic acid on chitosan was greater than that on chitin. Adsorption isothermal data could be interpreted by the Langmuir and Freundlich equation. Langmuir and Freundlich constants have been determined. The experimental data of the adsorption equilibrium from humic acid solutions correlate well with the Langmuir isotherm equation, as compared to the Freundlich isotherm equation. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2305–2310, 1998

INTRODUCTION

Chitin, poly(*N*-acetyl-D-glucosamine), a natural marine polymer and its deacetylated chitosan, poly(D-glucosamine) have been used in a variety of applied fields including biochemistry, pharmacology, medicine, wastewater management, and agriculture. Owing to the biodegradable and high adsorption capacities of chitin and chitosan, these polymers can be used in various applications in the effluent treatments or water samples. Many researchers have explored the possibility of using chitin for dye removal.[1–5] Chitosan has been used as an effective coagulation agent for suspended solids[6–8] and metal cation removal.[1,2,8–12] Apparently, no major studies have been done to clarify the humic acid in water sample using chitin and chitosan.

The yellowish-brown color of natural water comes from humic substances leached out from plant and soil organic materials. There is also some colloidal organic materials in natural water, and these colloids are humic acid. Humic acid consists of large molecules with molecular weights ranging from thousands to hundreds of thousands, and their structures are dominated by aromatic compounds. At present, there are several methods used to remove humic acid in natural water, including adsorption by kaolinite,[13] activate carbon,[14,15] ozone,[16] and coagulation using chemicals such as aluminium and ferric salts.[17]

In this study, the adsorption of humic acid onto chitin and chitosan were investigated in detail. Some of the physicochemical parameters of the adsorption were evaluated at the dynamic and equilibrium conditions.

EXPERIMENTAL

Materials

Sample of chitin and chitosan prepared from shells of prawns were kindly donated from Chitin–Chitosan Research Centre, Universiti Kebangsaan Malaysia, Malaysia. They were ground in a blender and sieved to a consistent particle size before use. All the reagents used were of analytical reagent grade. Doubly distilled water was used to prepare all the solutions.
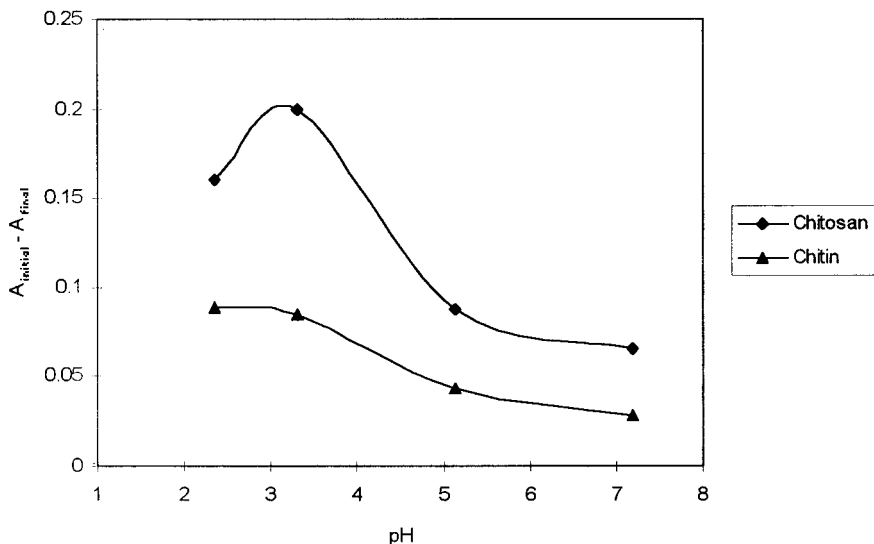
Figure 1 Effect of pH on the humic acid adsorption on chitin and chitosan: A, absorbance; A_{final}, final absorbance; $A_{initial}$, initial absorbance.

Methods

Stock solutions of humic acid were prepared by using humic acid (Fluka Chemika). These stock solutions were then diluted to give standard solutions of appropriate concentrations. Batch adsorption experiments were conducted in 500-mL beaker and equilibrated using a magnetic stirrer. 100 mL aliquots of each of these standard solutions were placed in 500-mL beakers and equilibrated with 0.100 g of chitin or chitosan. The equilibrated supernate was filtered from the polymer. The concentrations of humic acid were analyzed using ultraviolet-visible (UV–VIS) spectrometer (Metertek SP-850 model) at 420 nm.

The effect of humic acid removal was studied in the pH range of about 2–8. The pH of the initial solution was adjusted to the required pH value using either $0.10M$ HCl or $0.10M$ NaOH. Chitin or chitosan was equilibrated at the particular pH for about 30 min and at an initial humic acid concentration of 50 ppm.

The rate of adsorption was studied at above the optimum pH level and at the equilibration period of up to 30 min. Initial concentration of humic acid was 50 ppm.

Adsorption equilibrium studies were conducted using a contact time of 25 min at pH 3.07 for chitosan and at pH 2.40 for chitin. Isotherm studies were conducted with a constant chitin or chitosan weight (0.100 g) and varying initial concentration of humic acid in the range of 0–80 ppm.

The amount of adsorption was calculated based on the difference of the humic acid concentration in the aqueous solutions before and after adsorption, the volume of the aqueous solution (100 mL), and the weight of the chitin and chitosan (0.100 g).
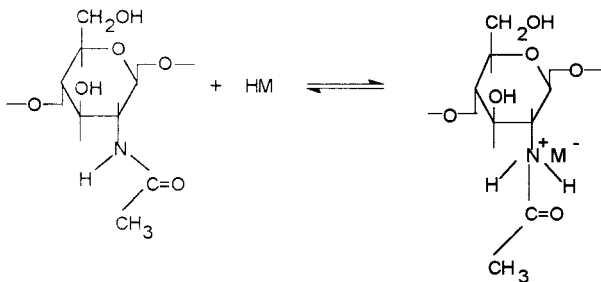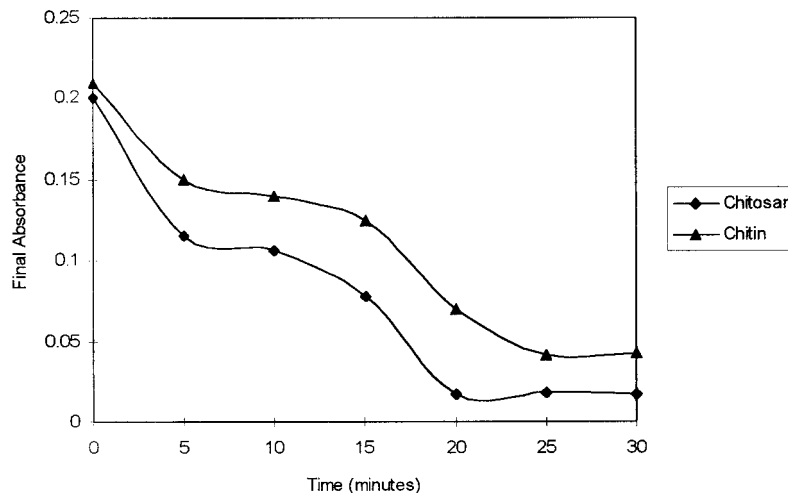

Chitin

Scheme 1

Chitosan

Scheme 2

Figure 2 The effect of the agitation period for the adsorption of humic acid on chitin and chitosan.

RESULTS AND DISCUSSION

The Effect of pH

The optimum pH for the adsorption of humic acid on chitin and chitosan can be observed by the change of the absorbance ($\Delta A = A_{\text{initial}} - A_{\text{final}}$) of the humic acid solution before and after adding chitin or chitosan. The decrease in ΔA means the decrease in adsorption of humic acid. The effects of pH on humic acid adsorption on chitin and chitosan decreased as the pH increased from about 3 to 7, as shown in Figure 1. A sharp decrease in the removal of humic acid was observed at pH

between 3 and 5. The maximum adsorption of humic acid on chitosan and chitin was found at pH 3.07 and 2.40, respectively. From Figure 1, a knowledge of pH is important in this study because of the dependence of the adsorption of humic acid on pH. The adsorption of humic acid on chitin and chitosan decreased above pH 3. The adsorption of humic acid by chitin and chitosan can be suggested as follows. The acetamido ($-\text{NHCOCH}_3$) groups of chitin were the only adsorptive groups because the hydroxyl group of ether on the glucosidic rings are protected by the solvated water, and the humic acid reaction can be shown in Scheme 1.
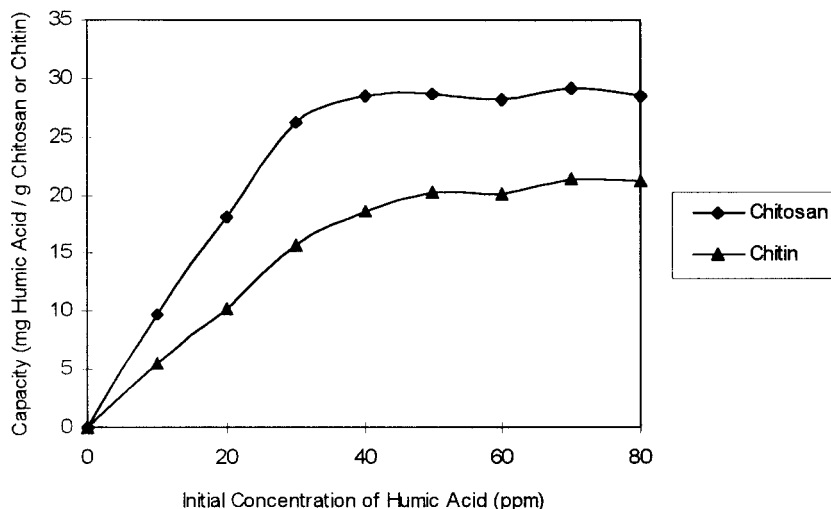

Figure 3 Adsorption of humic acid adsorbed on chitin and chitosan as a function of initial concentration.
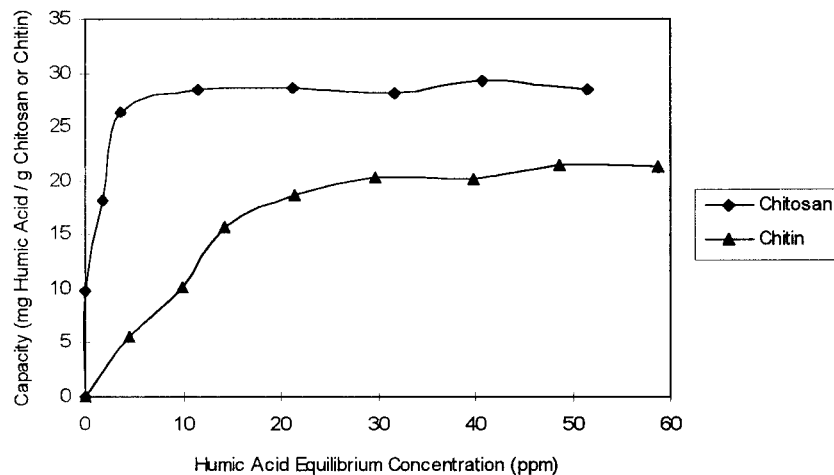
Figure 4 Adsorption isotherms of humic acid on chitin and chitosan.

In chitosan, the amine groups react with the humic acid, as shown in Scheme 2, where HM is the humic acid.

Agitation Period

The optimum period for the adsorption of humic acid on chitin and chitosan can be observed by looking at the final absorbance of humic acid solution after adding chitin or chitosan. The decrease in final absorbance means the increase in adsorption of the humic acid. Final absorbance of humic acid solution after adding chitin and chitosan as a function of time is shown in Figure 2. Results showed that the removal of humic acid increase with time, with more than 80% of total removal

being within 25 min. The color of the chitin and chitosan changed from pale white to yellowish-brown on adsorption of humic acid. Figure 2 can also explain in terms of the adsorption rate of humic acid. The rate of adsorption of humic acid onto chitin and chitosan was followed by looking at the decrease in the final absorbance of humic acid as a function of time until the final absorbance of humic acid remained constant; implying equilibrium has been reached. The gradual decrease in final absorbance of humic acid solution (increase in adsorption) was observed, and, after about 20 and 25 min for chitosan and chitin, respectively, a gradual approach to the limiting adsorption was observed. Therefore, the optimum agitation period of humic acid about 20 and 25
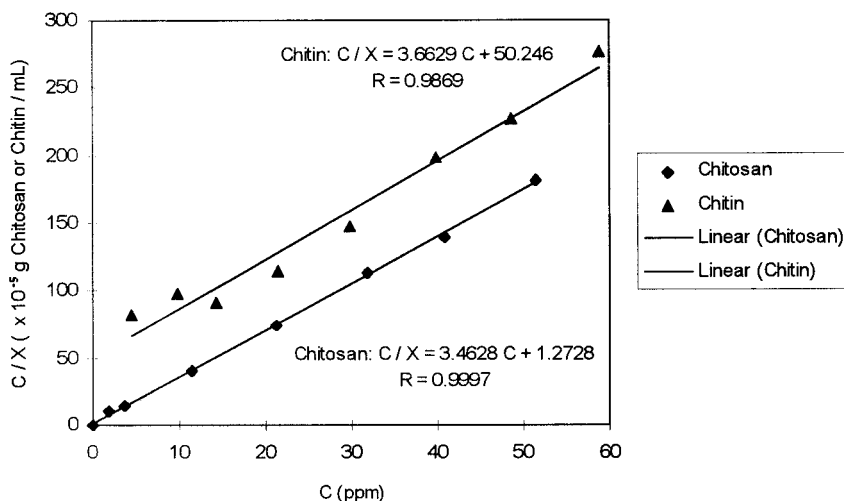

Figure 5 Adsorption isotherms of humic acid on chitin and chitosan, linearized according to the Langmuir equation.

Table I   Langmuir Isotherm Constants

Adsorption Constant	Chitin	Chitosan
X_{max} (mg humic acid/g)	27.30	28.88
b (mL/mg humic acid)	72.90	2720.70

min for chitin and chitosan, respectively. Chitin and chitosan can be considered porous polymers; therefore, humic acid can adsorp on the internal surface as well as the external surface. If the solution is stirred, the adsorption rate will be controlled by the rate of diffusion of humic acid into the pores of the chitin and chitosan.

Adsorption Equilibrium

The adsorption of humic acid as a function of the initial concentration of humic acid is shown in Figure 3. It is evident from this figure that the adsorption of humic acid on chitosan is significantly greater than that on chitin. The adsorption increases with an increasing initial concentration and approaches a constant value, which is found to be 50 and 40 ppm for the chitin and chitosan, respectively. The adsorption isotherms of humic acid onto chitin and chitosan are shown by the curve in Figure 4. It can be seen that the adsorption capacity increases as the concentration of humic acid increases until an equilibrium concentration of 30 and 10 ppm for chitin and chitosan, respectively, is reached. It suggests that the adsorption of humic acid on the chitin and chitosan are only to a certain amount. From this figure,

the maximum adsorption capacities of humic acid onto chitin and chitosan were about 20 and 28 mg/g, respectively. The significant conclusion was that the adsorption of humic acid on chitin was only about 71% of that on chitosan.

The experimental values of the isotherm were used in the linear forms of Langmuir equation, which is expressed by the following equation:

$$\frac{C}{X} = \frac{C}{X_{max}} + \frac{1}{X_{max}b}$$

where X is the amount of humic acid adsorbed per unit weight of chitin or chitosan at equilibrium concentration (mg/g), C is the equilibrium or final concentration (ppm), X_{max} is the maximum adsorption at monolayer coverage (mg/g), and b is the adsorption equilibrium constant (mL/mg) and is a measure of the energy of adsorption. Figure 5 shows the experimental adsorption isotherm values fitted into the linearized forms of Langmuir equation. From the slope and intercept of Langmuir isotherms, the numerical values of Langmuir isotherm constants were summarized in Table I.

The experimental values of the isotherm were also used in the linear forms of Freundlich equation, which is expressed by the following equation:

$$Log\ X = \frac{1}{n} Log\ C + Log\ P$$

where X and C were as described before, P is a constant and represents the adsorption capacity

Chitosan: Log X = 0.1457Log C + 4.2538
R = 0.9667

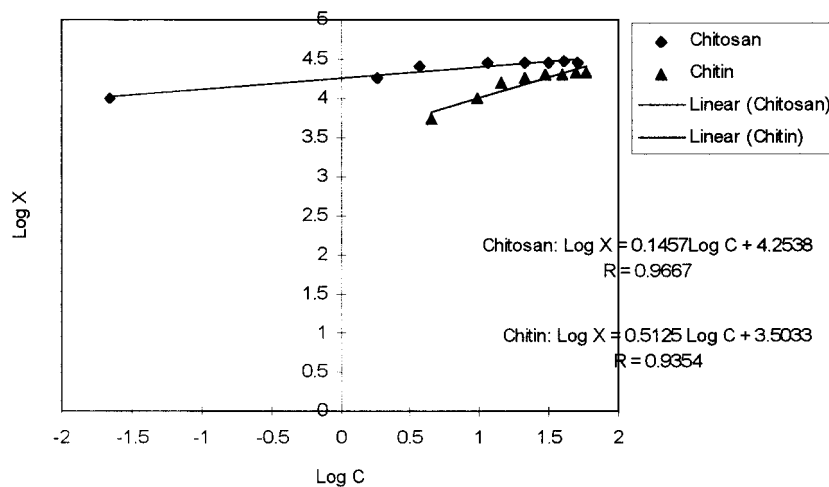Chitin: Log X = 0.5125 Log C + 3.5033
R = 0.9354

Figure 6 Adsorption isotherms of humic acid on chitin and chitosan, based on the linearized form of the Freundlich equation.

Table II Freundlich Isotherm Constants

Adsorption Constant	Chitin	Chitosan
P (mg humic acid/g)	3.19	17.93
n	1.95	6.86

(mg/g), while n is also a constant and represents the adsorption intensity. The isotherms for humic acid adsorption based on the linearized Freundlich equation is shown in Figure 6. As can be seen in Figure 6, the experimental values also fitted into the linearized form of Freundlich. The Freundlich isotherm constants obtained are summarized in Table II.

Correlation coefficients were calculated to be 0.9869 and 0.9997 for chitin and chitosan, respectively, for the Langmuir equation plot; meanwhile, the values for the Freundlich equation plot are 0.9359 and 0.9666 for chitin and chitosan, respectively. This indicates that the Langmuir relationship gives a better fit to the experimental values than the Freundlich.

The essential features of Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor, R, which is expressed by the following equation[18]:

$$R = \frac{1}{1 + bC_0}$$

where C_0 is the initial concentration of humic acid (ppm), and b is Langmuir's constant (mL/mg). The value of R was calculated to be 0.578 and 0.035 using 10-ppm humic acid concentration for chitin and chitosan, respectively. These results showed that chitin and chitosan are favorable adsorbers.[19]

CONCLUSION

The ability of chitin and chitosan to adsorb humic acid has been studied. The adsorption capacities at room temperature (27°C) of humic acid are 27.30 chitin and 28.88 mg/g chitosan. Thus, chitin and chitosan can be used to remove humic acid from water.

REFERENCES

1. R. A. A. Muzzarelli, *Natural Chelating Polymers,* Pergamon Press, Oxford, 1973.
2. R. A. A. Muzzarelli, *Chitin,* Pergamon Press, Oxford, 1976.
3. G. McKay, H. S. Blair, and J. R. Gardner, *J. Appl. Polym. Sci.,* **27,** 3043 (1982).
4. D. Knorr, *J. Food Sci.,* **48,** 36 (1983).
5. H. Yamamoto, *Makromol. Chem.,* **185,** 1613 (1984).
6. W. A. Bough, *J. Food Sci.,* **40,** 297 (1975).
7. W. A. Bough and D. R. Landes, in *Proceedings of the First International Conference on Chitin and Chitosan,* R. A. A. Muzzarelli and E. R. Pariser, Eds., MIT Sea Grant Report 78-7, Cambridge, 1978, p. 218.
8. M. B. Zakaria, M. J. Jais, A. Alimuniar, Z. Harahap, and W. S. W. Ngah, in *Chitin and Chitosan, The Versatile Environmental Friendly Modern Material,* M. B. Zakaria, W. M. W. Huda, and M. P. Abdullah, Eds., UKM Press, Malaysia, 1995, p. 275.
9. C. Peniche-Covas, L. W. Alvarez, and W. Arguelles-Monal, *J. Appl. Polym. Sci.,* **46,** 1147 (1992).
10. K. Inoue, Y. Baba, and K. Yoshizuka, *Bull. Chem. Soc. Jpn.,* **66,** 2915 (1993).
11. R. A. A. Muzzarelli and O. Tubertini, *Talanta,* **16,** 1571 (1969).
12. W. S. W. Ngah and I. M. Isa, *J. Appl. Polym. Sci.,* **67,** 1067(1998).
13. J. A. Davis, *Geochim. Cosmochim. Acta,* **46,** 2381 (1982).
14. J. J. McCreary and V. L. Snoeyink, *Water Res.,* **14,** 151 (1980).
15. W. J. Weber, T. C. Voice, and A. Jodellah, *J. Am. Water Works Assoc.,* **75,** 612 (1983).
16. A. P. Meijers, *Water Res.,* **11,** 647 (1976).
17. D. S. Babcock and P. C. Singer, *J. Am. Water Works Assoc.,* **75,** 8 (1979).
18. K. R. Hall, L. C. Eagleton, A. Acrivos, and T. Vermeulen, *Ind. Eng. Chem. Fundam.,* **5,** 212 (1966).
19. V. J. P. Poots, G. McKay, and J. J. Healy, *J. Water Pollut. Control Fed.,* **50,** 926 (1966).