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Equilibrium and Kinetic Study of Pepcidine Adsorption onto Humic Acid-Coated Nanoparticles

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In aquatic environments, humic acid (HA) was found to have a good ability for stabilizing nanoparticles. In this study, humic acid was extracted from Egyptian soil and was used to fabricate novel humic acid-coated TiO_2 nanoparticles (TiO_2/HA, 30 nm) by co-precipitation method. The deionized phenolic groups of humic acid were adsorbed on the surface of nano-TiO_2 and generate high charge density and strong interparticle repulsive forces that stabilize those nanoparticles. The great sorption capacity of TiO_2/HA nanoparticles was applied to remove pepcidine, as a model organic environmental contaminant from wastewater. The TiO_2/HA nanoparticles were characterized by FTIR and TEM techniques. The parameters influencing the pepcidine removal efficiency such as adsorbent dose, pH, initial adsorbate concentration and contact time were considered for optimal experimental conditions. The experimental results demonstrated that the investigated adsorption system complied well with Langmuir and pseudo second order kinetic models.

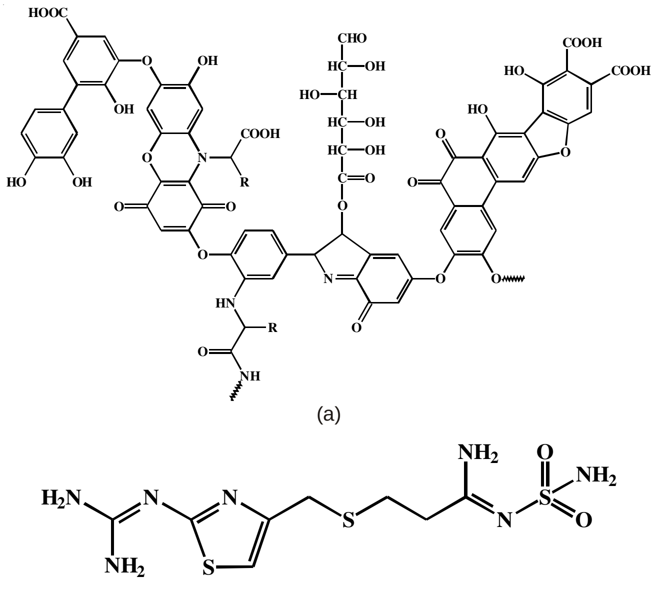
Keywords: Adsorption, Pepcidine, Humic acid, TiO_2, Nanoparticles.

INTRODUCTION

Humic acid is an abundant natural macro-biomolecule as a result of the decomposition of plants and animal residues[1]. Humic acid is a reactive polyelectrolytic molecule with unique amorphous structure consisting of large polycyclic aromatic hydrocarbons as a framework, on which various organic functional groups are located (Fig. 1a)[2-4]. Manufactured nanoparticles have remarkable optical, surface chemical and electronic properties and thus possess high adsorption capacity for both metals and organic contaminants. The good adsorptive properties of humic acid combined with the high adsorption capacity of TiO_2 nanoparticles, owing to their large specific surface areas can be used to manufacture novel nanoparticles for beneficial removal of toxic substances from aquatic environment. The deionized humic acid-phenolic groups can adsorb on nano-TiO_2 surface and stabilize its nanoparticles due to generating high charge density and strong interparticle repulsive forces[5]. Pharmaceuticals as contaminants in surface waters, wastewaters and drinking waters, which are originated from municipal wastewater, treatment plant of pharmaceutical production facilities, hospital effluent, aquaculture and landfills cause potential health risks for humans and biota. Pepcidine *i.e.*, 3-[({2-[(diaminomethylidene)amino]-1,3-thiazol-4-yl}-methyl)sulfanyl]-N'-sulfamoylpropanimidamide (Fig. 1b) is a histamine H_2-receptor antagonist that is a potent inhibitor of gastric and acid secretion in humans. As a continuation of using biomaterials and nanoparticles for removing hazardous materials from wastewaters[2-4,6-10], this study aimed at synthesizing, novel humic acid-coated TiO_2 nanoparticles by co-precipitation method for application to remove pepcidine, chosen as a model organic environmental contaminant from wastewater. The structure and morphology of the fabricated TiO_2/HA adsorbent were characterized by FTIR and TEM techniques. Different analytical parameters influencing the pepcidine removal efficiency including adsorbent dose, pH, initial adsorbate concentration and contact time were investigated. Various adsorption isotherm and kinetic models are applied to the experimental data to establish the best fitting models.

EXPERIMENTAL

The chemicals used throughout this work are of analytical reagent quality. Deionized water was used for preparing solutions and the pH was adjusted by adding HCl and NaOH to solutions and measured using a Jenway Model 3510 pH meter. A Solution (100 mg/L) of pepcidine (by Johnson &



(a)

(b)

Fig. 1. Chemical structure of (a) humic acid building block (b) pepcidine

Johnson/Merck) is prepared using deionized water and ultrasonicated (Bransonic 5510 E-Mt) for 0.5 h. Anatase TiO_2 nanopowder (99+ %, 10-25 nm, 250 m^2/g) was supplied from the US Research Nanomaterials, Inc.. Humic acid is extracted and characterized by the same methods as described[4].

Preparation of HA/TiO_2: The humic acid solution was prepared by dissolving 3 g of humic acid in 300 mL Na_2CO_3 solution (0.1 M, pH = 8.5), stirred for 6 h and filtered to remove the residual undissolved humic acid. Then100 mg of nano-TiO_2were added to 100 mL of this humic acid solution, shaken at 150 rpm (Experimental Equipment Co.) for 1 h and centrifuged (5810R, Eppendorf, Germany) at 12,000 rpm for 0.5 h. The precipitated material was rinsed with deionized water for three times, freeze-dried, grounded and collected and stored in sealed glass vials for use.

Characterization of TiO_2/HA nanoparticles: TiO_2/HA nanoparticles were characterized by FTIR spectrophotometer model 8400S (Shimadzu, Japan) to investigate the functional groups on the surface. The morphology of TiO_2/HA nanoparticles was performed by TEM (H-7500, Hitachi, Japan).

Adsorption experiments: Batch mode experiments were conducted to investigate the adsorption of pepcidine onto TiO_2/HA at pre-adjusted conditions using aliquots of 20 mg adsorbent samples added to 100 mL of pepcidine solutions with different initial concentrations (0-100 mg/L) in 250 conical flasks sealed with parafilm and shaken at 150 rpm in the dark at 25 °C for 1 h. The solutions of pepcidine were prepared by dissolving the calculated amount of adsorbate in 1 L of deionized water and ultrasonicated (Bransonic 5510 E-Mt) for 0.5 h. 3 mL samples were taken, centrifuged and analyzed using double beam UV/visible spectrophotometer (CE 7400). The experiments were done in triplicate and the average is used in calculations. The adsorbed pepcidine, q (mg/g) was calculated from the difference in concentration using eqn. 1.

$$q = \frac{(C_o - C_f)V}{W} \qquad (1)$$

where C_o and C_f (mg/L) are the initial and final substrate concentrations, V (L) is the volume of substrate in solution and W (g) is the mass of TiO_2/HA.

Adsorption kinetics experiments: The same batch adsorption experiments were performed at predetermined time intervals for adsorption kinetic studies and eqn. 1 was applied at each time interval.

Effect of analytical parameters (pH, initial adsorbate concentration, adsorbent dose, contact time): The same method in batch adsorption experiments were performed to investigate the effects of different analytical parameters on the adsorption where the pH of adsorption systems was adjusted to 3, 5, 7, 9 and 11 to study the effect of solution pH, the pepcidine concentrations (0, 20, 40, 50, 60, 80 and 100 mg/L) were used to investigate the effect of initial adsorbate concentration, different pepcidine doses (10, 20 and 50 mg) were utilized to investigate the effect of adsorbent dose and the adsorption of pepcidine on TiO_2/HA at various contact times (20, 40, 60 and 100 min) was studied to search for the effect of contact time.

Langmuir model calculation: The percent adsorption was evaluated from eqn. 2:

$$\text{Adsorption } (\%) = \frac{C_o - C_f}{C_o} \times 100 \qquad (2)$$

The mass of pepcidine sorbed onto1g of TiO_2/HA, q_i (mg g^{-1}) in in binding step-i can be represented by Langmuir isotherm[11] (eqns. 3-5).

$$q_i = \frac{K_i \nu_i c}{1 + K_i c} \qquad (3)$$

$$\frac{1}{q_i} = \frac{1}{\nu_i} + \frac{1}{K_i \nu_i c} \qquad (4)$$

$$\frac{c}{q_i} = \frac{c}{\nu_i} + \frac{1}{K_i \nu_i} \qquad (5)$$

where c (mg L^{-1}) is the equilibrium concentration of pepcidine, K_i is the conditional equilibrium constant and ν_i is the stoichiometric site-i capacity (mg g^{-1}). The plot of c/q_i *vs.* c can reveal how many steps are involved in the adsorption process (eqns. 2-4). From the slope and intercept of the linear segments in the plots of eqns. 4 and 5, and can be estimated for each adsorption step.

RESULTS AND DISCUSSION

Characterization of TiO_2/HA nanoparticles: The FTIR spectra of anatase TiO_2, TiO_2/HA and humic acid particles are shown in Fig. 2a-c. The peaks (OH- or NH-stretching) observed at 3446 cm^{-1} for anatase TiO_2 and at 3419 cm^{-1} for humic acid, were shifted to 3392 cm^{-1} due to humic acid coating in TiO_2/HA nanoparticles (Fig. 2d). The peak (Ti-O bond) observed at 516 cm^{-1} for anatase TiO_2 was shifted to 478 cm^{-1} due to the formation of TiO_2/HA nanoparticles. Also, the peaks (C=C, C=O, COO- groups stretching) observed in the 1650-1615 cm^{-1} region were affected by humic acid coating. The morphology of TiO_2/HA nanoparticles, Fig. 3 was studied using TEM imaging which demonstrated that the shape of the fabricated

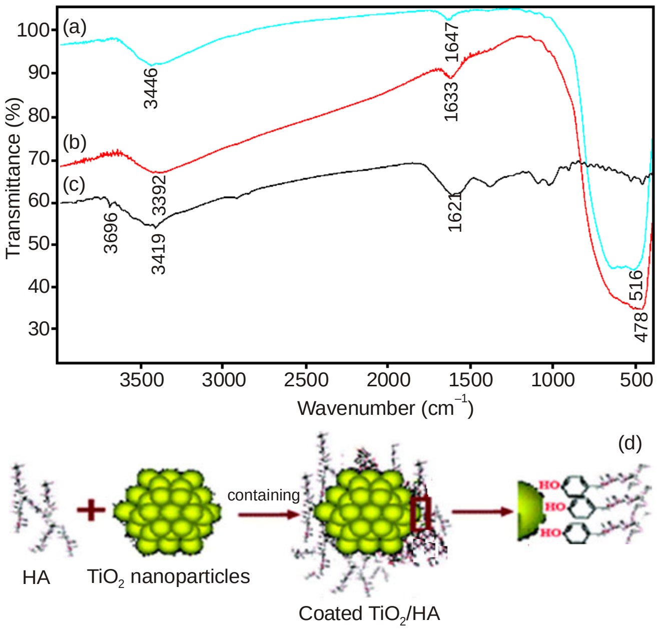


Fig. 2. FTIR spectra of (a) anatase TiO_2(b) TiO_2/HA (c) humic acid (d) coating of humic acid on nano-TiO_2

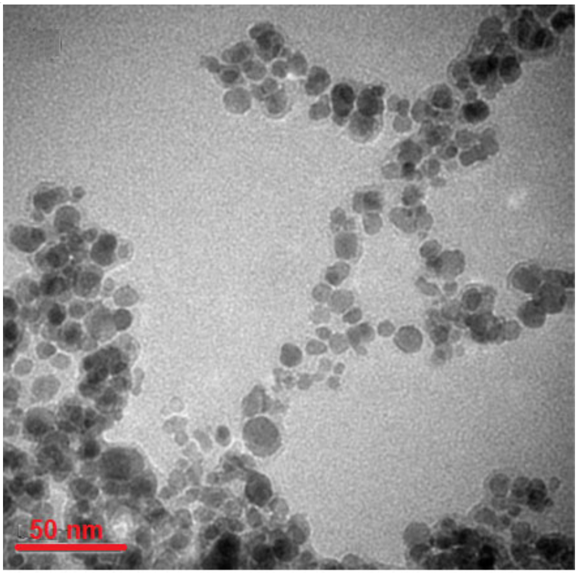


Fig. 3. TEM image of TiO_2/HA nanoparticles

nanoparticles was quasi-spherical and had nearly uniform distribution of particle size (10-12 nm). It is observed that humic acid can stabilize nano-TiO_2 due to the steric repulsion caused by the electro-repulsion of humic acid functional groups.

pH effect on the adsorption: The pH effect on the adsorption amount of pepcidine, q_e (mg g^{-1}) onto TiO_2/HA nanoparticles (Fig. 4) showed that the adsorbed amount increased sharply from pH 5 to 9. The pH usually changes the surface electric charges of the adsorbent and reduces or facilitates the adsorbent-adsorbate electrostatic interaction[11]. Also, the humic acid-conformations vary with pH alternation, which influences the extent of adsorption[12-14]. The maximum adsorption was shown at pH 8.5 because the humic acid aliphatic chains on HA-TiO_2 structure condensed at pH > 7 and thus more adsorption sites will be available.

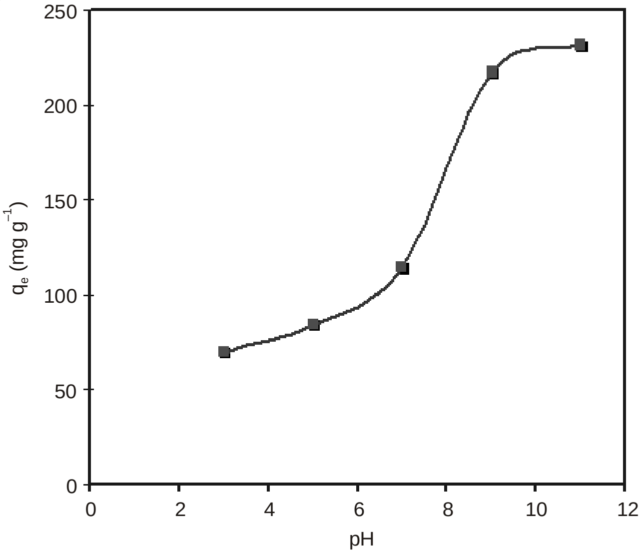


Fig. 4. Effect of pH on the adsorption of pepcidine onto TiO_2/HA nanoparticles at 25 °C

Effects of contact time, initial adsorbate concentration and adsorbent dose on the adsorption: From the experimental data, the adsorbent dose was selected to be 20 mg. The efficiency of the adsorption increases with contact time where during the first 40 min 80 % of pepcidine was adsorbed and the adsorption equilibrium was achieved within 60 min. Additionally the percent of adsorption increased with decreasing its initial concentration and the appropriate initial pepcidine concentration was 50 mg/L.

Adsorption isotherm: Langmuir isotherm[15] is a simple model that was used to explain different adsorption systems (eqns. 2-4). It suggested the occurrence of uniform adsorption to saturate the adsorbent active sites. The Langmuir isotherm for the adsorption of pepcidine onto HA/TiO_2 at pH 8.5 and 25 °C is shown in Fig. 5a. The linear plots of Langmuir model (eqn. 4 and 5) gave two linear segments, which means that the adsorption of pepcidine onto HA/TiO_2 at pH 8.5 and 25 °C was taken place in two adsorption steps A and B, Fig. 5b.These two adsorption sites have site capacities of ν_A and ν_B and conditional equilibrium constants of K_A and K_B, respectively, Table-1, which were calculated from the slope and intercept of each linear segment in Fig. 5b.

TABLE-1
ADSORPTION ISOTHERM AND KINETIC PARAMETERS AT pH 8.5 AND 25 °C

	Step (A)		Step (B)	
Langmuir adsorption parameters	ν_A (mg/g)	K_A	ν_B (mg/g)	K_B
	126.6	0.21	277.8	0.03
Pseudo-second-order model parameters	q_e (mg/g)	k_2 (g mg^{-1} min^{-1})		R^2
	376.5	0.0224		0.98

The linear plots in Fig. 5b prove the correctness of applying Langmuir model to describe the adsorption process, which occurred in two adsorption sites in HA/TiO_2 surface. The site capacity represents the sorbed amount of pepcidine when the adsorption site is fully occupied.

Adsorption dynamics: To examine the controlling mechanism and adsorption kinetics, the adsorption of pepcidine onto

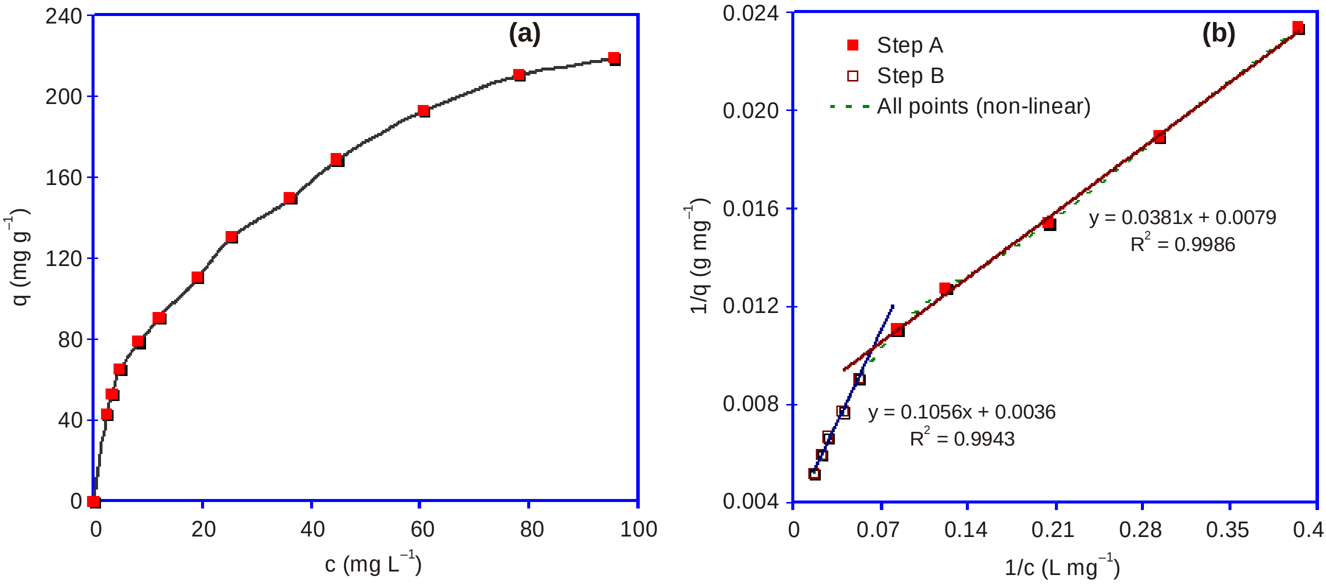


Fig. 5. (a) Langmuir isotherm for the adsorption of pepcidine onto HA/TiO_2 at pH 8.5 and 25 °C (b) linear segments observed in the plot of eqn. 4

HA/TiO_2 at different time intervals was investigated. The experimental adsorption kinetic data fitted well to the pseudo-second-order model, eqn. 6 based on the adsorption equilibrium capacity. This pseudo-second-order rate law is always well applied to adsorption systems, where the adsorption rate does not depend on the adsorbate concentration but on the sorption capacity[16,17].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{6}$$

where k_2 (g mg^{-1} min^{-1}) is the pseudo-second-order adsorption rate constant, q_e and q_t (mg g^{-1}) is the amount of pepcidine adsorbed onto HA/TiO_2 at equilibrium and the time of t (min), respectively. The value of q_t is calculated according to eqn. 1. The values of q_e and k_2 can be calculated from the slope and the intercept, respectively of the straight line obtained on plotting t/q_t *vs.* t (Table-1). The value of k_2 was found to be 2.24×10^{-2} g mg^{-1} min^{-1} while the value of q_e was 376.5 mg g^{-1}. The experimental data well fitted to the pseudo-second-order model ($R^2 = 0.98$) and this indicated that pepcidine adsorption capacity is proportional to the number of occupied HA/TiO_2 active sites and as the adsorption process proceeded, those active sites would decline. Therefore, the pepcidine adsorption rate was mainly dependent on the availability of those adsorption sites *i.e.* the unoccupied HA/TiO_2 active sites at any time.

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