



Isotherm and Thermodynamic Studies of the Biosorption of Humic Acid from Aqueous Solution by Pine Sawdust based Activated Charcoal

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Activated charcoal was prepared from pine tree sawdust by chemical activation by means of phosphoric acid (PSDP) that was used for Humic acid bio sorption from aqueous medium. The influence of humic acid initial concentration, sorbent mass, and solution temperature on sorption process was investigated. Langmuir and Freundlich isotherm models were used to analyze the equilibrium sorption data. The maximum adsorption capacities of PSDP obtained from Langmuir were 170.9, 182.1 and 209.6 mg/g at 25°C, 45°C and 65°C, respectively. Humic acid adsorption onto PSDP was spontaneous, favorable at higher temperature and endothermic in nature. Activated charcoal from pine tree sawdust proves to have high capacity adsorptive to natural organic compound (humic acid).

Keyword: Chemical Activation, Freundlich isotherm, Langmuir isotherm, Pine Tree Sawdust, Sorption

Introduction

Water is extremely important and is a lasting element for human survival. Clean and healthy water ensures elimination of compounds that causes bad smell, taste and color. The color in crude water generally owes to the color of organic matter (principally fulvic acid and humic acid), combined with soil humus fraction, according to the World Health Organization.¹ Humic acid is the fraction of humic compounds that are soluble above pH 2 in water.² The molecules of humic acid are complex and contain various functional groups, such as phenol, ketone, carboxylic, quinonyl, amino, ester and hydroxyl.³ Humic acid's molecular weight is between 1 to 5 kDa. The most abundant functional group responsible for charging humic acid in medium molecules is the carboxylic and phenolic groups.⁴ During water purification, halo acetic acids and trihalomethanes are formed due to the reaction of humic substances with chlorine. Humic substances helps in increasing the transportation of heavy metal and organic pollutants through the binding with humic acid, which results in growth of bacteria and uncomfortable taste and color.⁵ It must avoid its impact on human health. Thus, natural organic matters must be eliminated from water before the

chlorination process.⁶ Conventional techniques are widely used to eliminate humic substances such as coagulation,⁷ ion exchange,⁸ advanced oxidation process,⁹ membrane filtration¹⁰ and adsorption.¹¹ Its low cost, simplicity, high-efficiency and ease of regeneration make adsorption one of the most effective methods. There are many sorbents used to remove humic substances from aquatic environments such as commercial activated biochar,¹² resin,¹³ chitosan,¹⁴ iron oxides,¹⁵ graphene oxide¹⁶ and nano graphene.^{3b} The above sorbents are effective, but expensive, and costs for higher quality are greater. Therefore, researchers need to find sorbents that are more efficient and cheaper. Sawdust is a promising low cost and available natural lignocellulosic sorbent that can be used in pollution removal from wastewater such as colors,¹⁷ phenol¹⁸ and heavy metals.¹⁹

However, most of natural sorbents have low capacity for adsorption, which is a main restriction to use the min processes of water treatment. Nevertheless, the chemical modification can be conducted to elevate the adsorptive capacity of sorbents through adding other functional groups to the sorbent surface or via elevating their porosity. In present work, pine tree sawdust was modified by phosphoric acid treatment followed by pyrolysis at 600°C to obtain pine sawdust activated charcoal (PSDP). The physico-chemical properties of prepared

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sorbent were performed using several analytical techniques. The efficiency of PSDP for humic acid removal was studied. The influence of sorbent dose, humic acid initial concentration and temperature were examined. The findings from adsorption of humic acid on PSDP were modeled using isotherms and thermodynamic models.

Materials and Methods

Preparation of Adsorbate

All chemicals and reagents used throughout this work were of analytical grade. Humic acid stock solution (500 mg/L) was prepared by dissolving the desired amount of humic acid (sodium salt) in 100 mL of deionized water. Different initial concentrations (50–500 mg/L) of humic acid were prepared from stock solution by dilution with deionized water.

Preparation of Activated Charcoal

Pine tree sawdust was initially washed with deionized water to eliminate surface dust and dirt. After drying in an oven at 120°C for 72 h, it was ground and then 30 g were impregnated in 50 ml of 80 vol. % phosphoric acid and left for 24 h. The impregnated solid was oven dried at 80°C overnight. The dried sample was placed into the tube of a tubular electric furnace at 2.5 °C/ min up to 600°C for 100 min. Pine sawdust-based activated charcoal (PSDP) sample was gradually cooled to room temperature. It was then washed with hot deionized water until the pH of wastewater become neutral followed by drying in an oven at 120°C for 24 h.

Characterization of Activated Charcoal

The BET surface area of the PSDP was measured using nitrogen sorption at 77 K utilizing (NOVA 1000e Quantacrome, USA). Chemical properties of PSDP were determined using Fourier Transform Infrared Spectroscopy (FTIR-100, Shimadzu) in 4000–400 cm⁻¹ range and KBr disk.

Adsorption Experiments

Adsorption experiments were carried out using various weight (0.05–4 g/L) PSDP to 10 ml of different concentration (50–350 mg/L) of humic acid solution in 50 mL flask. The flasks were shaken in water-bath shaker at 250 rpm and 25°C. Adsorbent was separated by using Whatman 44 membrane filters. The concentration of humic acid was analyzed using UV-Vis Spectrophotometer (Perkin-Elmer model 550S) at λ_{max} = 375 nm. The mean values of

repeated three times of batch experiments were obtained.

The removal rate (*R*%) was calculated using Eq. 1 and the adsorption capacity, *Q_e* (mg/g), was assessed from the following Eq. 2:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad \dots (1)$$

$$Q_e = \frac{V(C_0 - C_e)}{M} \quad \dots (2)$$

where *C₀* and *C_e* (mg /L) is the humic acid initial and final concentration respectively, *V*(L) is the solution volume and *M* (g) is the adsorbent mass.

Results and Discussion

Characteristics of Prepared Activated Charcoal

The BET surface area and total pore volume of PSDP is 999 m²/g and 7.385e⁻⁰¹ cm³/g respectively. FT-IR spectrum of PSDP (Fig.1), shows peaks at 3401 and 1080 cm⁻¹ due to the OH vibrations which indicate the existence of surface hydroxyl groups. The presence of a peak at 3401 cm⁻¹ might be because of both free and hydrogen bonded OH groups. The triplet in peaks detected in the range (1200–1000 cm⁻¹) results from superposition of C – OH bond vibrations. Triple bonds and other restricted forms of functional groups were typical for absorption peaks at the range (2377–2310 cm⁻¹). Approximately, the peak at 1685.7 cm⁻¹ is commonly resulted from the stretching C = O vibration in ketones, lactones, aldehydes and carboxyl groups. This peak might be slightly overlapping with an aromatic C=C ring stretching vibration peak at 1556.6 cm⁻¹.

Factors Affecting the Removal Process

Effect of Sorbent Mass

The sorbent mass is a significant factor for increasing humic acid adsorption. The effect of sorbent mass in the range 0.5–4 g/L was studied and the findings are shown in Fig. 2.

Initially, removal percentage raised rapidly as adsorbent dose increased but the capacity for adsorption (*Q_e*) reduced. The humic acid removal percentage was increased and decreased sorption capacity for PSDP which owing to the availability of higher active sites onto surface of sorbent causing from the elevation of mass and conglomeration of the sorbent.²⁰

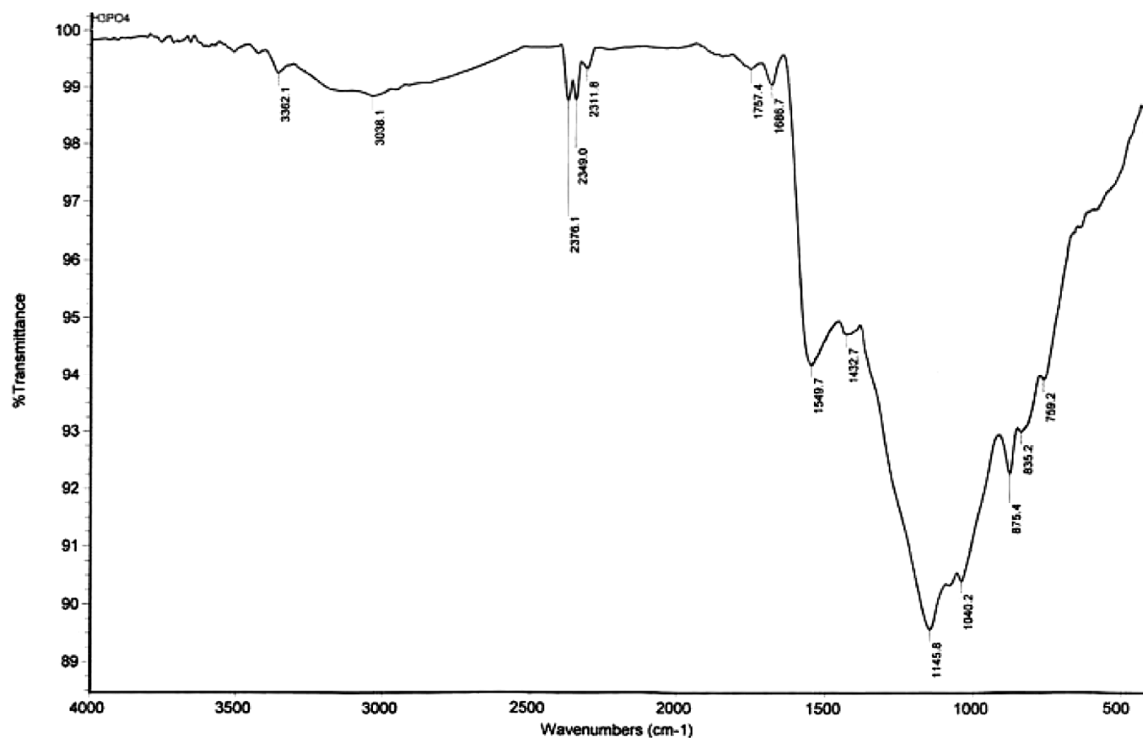
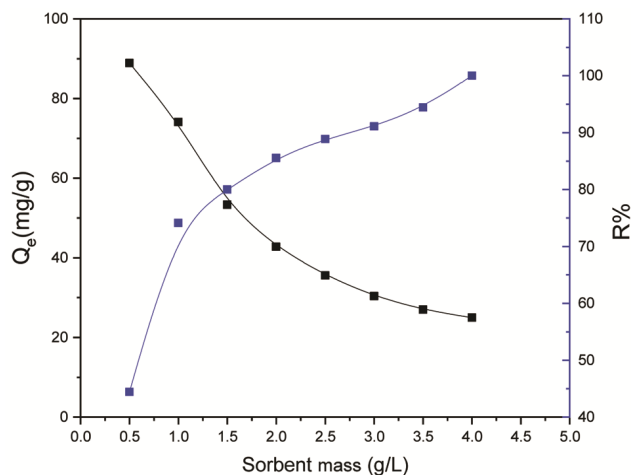
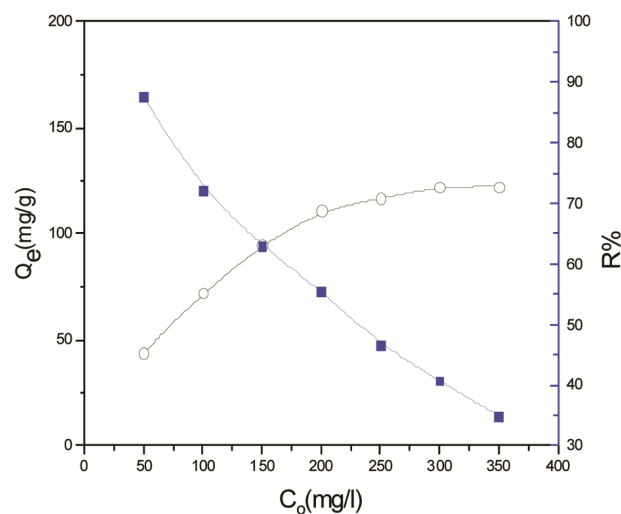


Fig. 1 — FT-IR spectra of prepared activated charcoal

Fig. 2 — Effect of sorbent dose uptake and % of removal on humic acid adsorption. Experimental conditions employed (V) = 10 mL; pH=3.5; (M) = 0.05–4 g/L; (C_0) = 100 mg/L; (T) = 25°C

Effect of Humic Acid Initial Concentration

The effect humic acid initial concentration on adsorption performance was examined, and the findings are presented in Fig 3. The humic acid percent removal efficiency decreased when its initial concentration raised from 50 to 350 mg/L while the adsorption capacity decreased. By keeping constant all other parameters under the highest optimal states. The reason was that active binding sites are reduced at

Fig. 3 — Influence of initial concentration on the equilibrium uptake (q_e) and % of removal on humic acid adsorption. Experimental conditions employed (V) = 10 mL pH=3.5; (M) = 1 g/L; (C_0) = 50–350 mg/L; (T) = 25°C

high initial concentrations but at humic acid lower concentrations is easier to bind to the PSDP because the binding area for humic acid is adequate.^{3a,21}

Equilibrium Adsorption Isotherms

Equilibrium adsorption isotherm studies are important for understanding the interaction between

the sorbates and sorbent in the aqueous medium.^{21,22} Equilibrium adsorption isotherm can be attained from a plot of Q_e (mg/g), which is the quantity of humic acid adsorbed versus C_e (mg/L), which is the concentration of humic acid after adsorption (Fig. 4). The isotherms are classified in four main isotherms groups according to Giles classification.²³ The humic acid adsorption isotherm is L type isotherm. The L type isotherm proposes that adsorbate and solvent are weakly competitive for adsorption locations.²⁴ This reveals that humic acid is strongly adsorbed onto the PSDP sorbent.

Adsorption Isotherms

Adsorption isotherms are utilized to explain the reaction of adsorption among sorbent and adsorbed material at equilibrium. The adsorption experimental data were assessed using Langmuir and Freundlich isotherms models that expressed as follows:

Langmuir equation²⁵

$$\frac{C_e}{Q_e} = \frac{1}{K_{Lan}Q_{Max}} + \frac{C_e}{Q_{Max}} \quad \dots (3)$$

Freundlich equation²⁶

$$\log Q_e = \log K_{Fre} + \frac{1}{n} \log C_e \quad \dots (4)$$

where C_e (mg/L) is the humic acid concentration after adsorption, Q_e (mg/g) is the amount of humic acid adsorbed at equilibrium, K_{Lan} (L/mg) is constant associated to adsorption free energy and Q_{Max} (mg/g) is theoretical maximum humic acid adsorption capacity. In the Freundlich adsorption isotherm, n and K_{Fre} (mg/g (L/g)^{1/n}) are the constants relative to

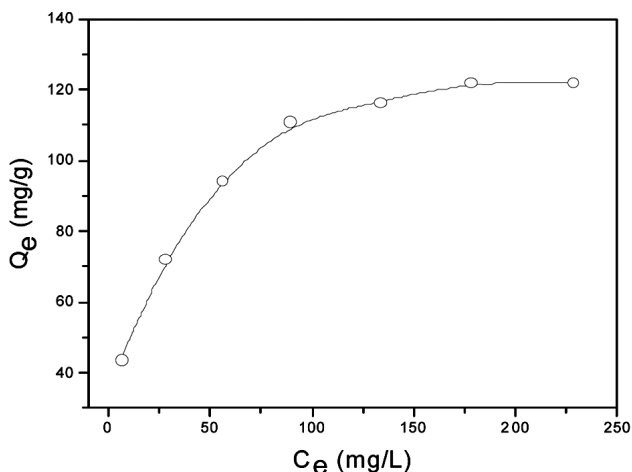


Fig. 4 — Equilibrium adsorption isotherms of humic acid on to PSDP

adsorption intensity and adsorption capacity, respectively. The Freundlich and Langmuir plots are shown in Fig. 5, and their parameters in addition to correlation coefficients (R^2) are tabulated in Table 1. From Table 1, The R^2 value of Langmuir isotherm

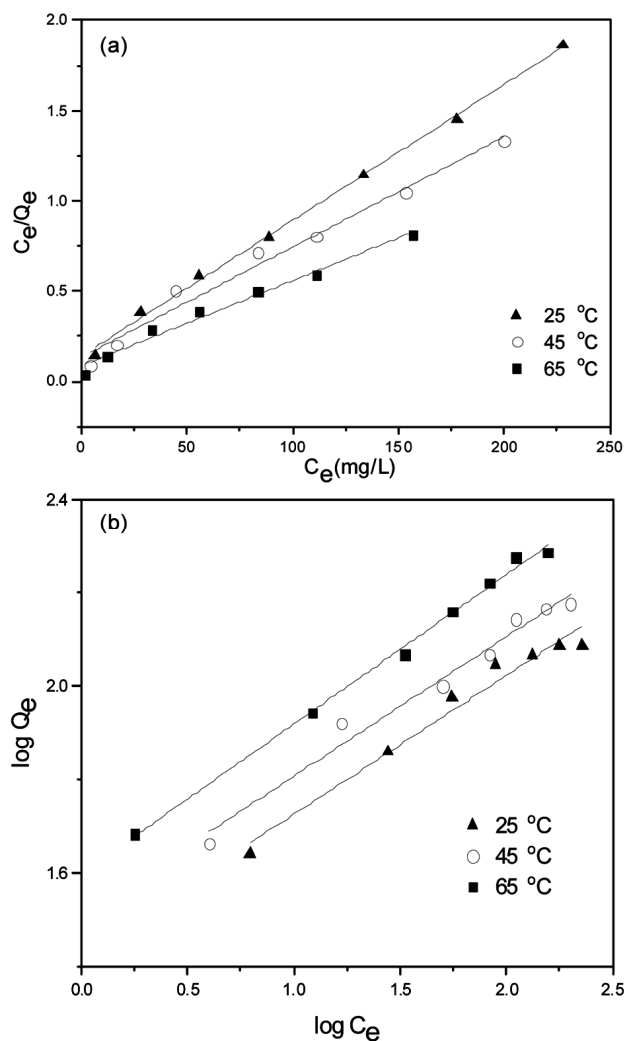


Fig. 5 — Adsorption isotherms plots of humic acid onto PSDP with the Langmuir adsorption model (a) and the Freundlich adsorption model (b)

Table 1 — Adsorption isotherms parameters of humic acid onto PSDPat different temperatures

	25°C	45°C	65°C
Langmuir			
Q_{Max} (mg/g)	170.9	182.1	209.6
K_{Lan} (L/mg)	0.028	0.04	0.05
R^2	0.997	0.978	0.988
Freundlich			
K_{Fre} (mg/g (L/g) ^{1/n})	21.3	30.4	39.8
n	2.6	3.04	3.1
R^2	0.963	0.970	0.984

was more than Freundlich isotherm. Thus, the humic acid adsorption on to PSDP well defined by the Langmuir isotherm. The calculated Q_{Max} of PSDP for humic acid were 170.9, 182.1 and 209.6 mg/g at 25°C, 45°C, and 65°C, in that order. Values of n are greater than one, which represented a favorable adsorption of humic acid on PSDP.²⁷ The adsorption capacities, Q_{Max} elevated as temperature elevation for PSDP indicating an endothermic adsorption.²⁸

Adsorption thermodynamics

Thermodynamic parameters including enthalpy (ΔH° , kJ/mol), free energy (ΔG° , kJ/mol), and entropy (ΔS° , J/mol K) for humic acid adsorption onto PSDP were computed according to the eq.²⁹

$$K^\circ = \frac{C_e}{C_0 - C_e} \quad \dots (5)$$

$$\ln K^\circ = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \quad \dots (6)$$

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \dots (7)$$

Where T (K) is the absolute temperature, R is the gas constant (8.314 J/mol K) and K° is the equilibrium constant. ΔH° and ΔS° values were calculated from the slope and intercept of Van't Hoff plot of $\log K^\circ$ vs. $1/T$ (Fig.6) and ΔG° values are from Eq. (7). Thermodynamic parameters values are recorded in Table 2. The humic acid adsorption onto PSDP is feasible and spontaneous due to the negative ΔG° values. Reduction in ΔG° value as temperature increases from (298 to 338K), representing that the adsorption process was encouraging at high temperature. The positive value of ΔH° confirmed that the adsorption reaction was endothermic in nature. The value of ΔS° was positive which revealed that PSDP prefer humic acid.³⁰

Comparison with other sorbents

Humic acid adsorption capacity onto PSDP must be contrasted with other sorbents to justify the weight of it as an effective sorbent. The Q_{Max} values for humic acid adsorption on various sorbents are contrasted to our sorbent and are presented in Table 3. PSDP exhibited higher Q_{Max} than other sorbents, which reflected that PSDP could be a talented sorbent for humic acid removal.

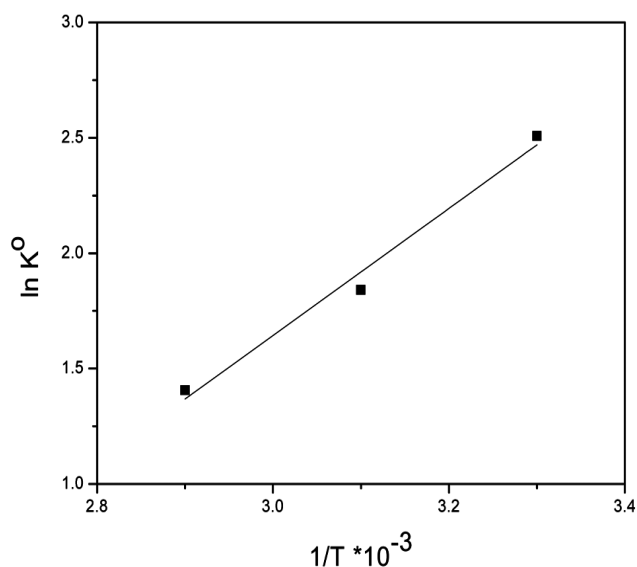


Fig. 6 — Van't Hoff plot of humic acid adsorption on PSDP carbon

Table 2 — Thermodynamic parameters of humic acid adsorption onto PSDP at a different temperature

Temperature K	K° (L/g)	ΔG° kJ/mol	ΔH° kJ/mol	ΔS° J/mol K
298	4	-3.468		
318	6.04	-4.758	22.89	55.19
338	12.18	-7.025		

Table 3 — A comparison of humic acid adsorption capacities by various sorbents

Adsorbent	Capacity (mg/g)	Adsorption conditions		Reference
		Humic acids	pH	
Activated carbon from rice husk	21–45	Fluka (sodium salt)	5	31
Metal-modified silica	1.5–3.6	Wako (purified)	n.a.	32
Metal-modified silica	0.2–3.6	Nordic (purified)	n.a.	32
Pillared bentonite	537	Aldrich (sodium salt)	4	33
Chitosan	57.14	Aldrich (sodium salt)	3.5	34
modified pumice stone with sulfuric acid	65.75	Merck Organics	3	3a
Activated sludge	2.4	Aldrich (sodium salt)	4.4	35
rice husk ash	2.7	Aldrich (purified)	6	36
aminopropyl functionalized rice husk ash	8.2	Aldrich (purified)	6	36
PSDP	170	Serva (sodium salt)	3.5	This work

n.a.: not available

Conclusions

Phosphoric acid activated pine sawdust charcoal (PSDP) was prepared and used in humic acid biosorption from aqueous medium. Phosphoric acid activated PSDP surface area increased up to 991.14 m²/g and the FTIR spectra revealed that PSDP carbon has different functional groups which increased humic acid adsorption. The Freundlich isotherm model defined the adsorption process with high correlation coefficient R², more than the Langmuir isotherm model. Langmuir maximum adsorption capacities of PSDP were 170.9, 182.1 and 209.6 mg/g at 25°C, 45°C, and 65°C, respectively. From thermodynamic data, it was found the adsorption process was spontaneous, favorable and endothermic. Thus, present study results indicate that PSDP can be efficiently applied humic acid removal from aqueous solutions.

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