Activated Tea Waste as a Potential Low-Cost Adsorbent for the Removal of *p*-Nitrophenol from Wastewater

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The aim of this work was to determine the potential of activated tea waste (ATW) as a useful adsorbent for the removal of *p*-nitrophenol (*p*-NP) from aqueous systems. The study was realized using batch experiments with synthetic wastewater having a *p*-NP concentration of 1000 $\text{mg}\cdot\text{L}^{-1}$. The effects of pH, contact time, and presence of anions were investigated. An increase in the pH to above neutrality resulted in a decrease in the *p*-NP adsorption capacity. The adsorption process reached equilibrium within 5 h of contact time. The Freundlich, Langmuir, Temkin, Dubunin−Radushkevich, and Redlich−Peterson adsorption models were used for mathematical description of the adsorption equilibrium, and it was found that the experimental data fitted very well to the Langmuir isotherm. Batch adsorption studies, based on the assumption of a pseudo-first-order, pseudo-second-order, or intraparticle diffusion mechanism, showed that the kinetic data followed closely a pseudo-second-order rather than a pseudo-first-order mechanism. The adsorption capacity of ATW for the removal of *p*-NP was found to be 142.85 $\text{mg}\cdot\text{g}^{-1}$. These results clearly indicate the efficiency of activated tea waste (ATW) as a low-cost adsorbent for treatment of wastewater containing *p*-NP.

Introduction

The presence of phenolic compounds in waste effluent streams is of growing concern due to their relatively high toxicity. Nitrophenols are of interest, as they are listed as priority toxic pollutants by the United States Environmental Protection Agency.[1] The world production of nitrophenol derivatives is continuously growing. It is mainly used to prepare drugs, fungicides, dyes, darkening leathers, etc.[2] *p*-Nitrophenol (*p*-NP), however, is associated with some undesirable properties like irritation of the eyes, skin, and respiratory tract and may cause inflammation of those parts. The Ministry of Environment and Forests (MOEF), Government of India, and EPA, USA, have listed phenol and phenolic compounds on their priority pollutants lists. Their removal from surface water and groundwater is hindered due to their high stability and solubility in water as well as their resistance to traditional water purification methods[3] apart from the adsorption method. Various abatement technologies for phenolic derivatives from wastewater have been proposed in the literature.

They include separation by steam-distillation, extraction, adsorption, membrane pervaporation,[4] membrane-based solvent extraction, destruction by catalytic wet air oxidation,[5] oxidation with ozone, hydrogen peroxide, chemical oxidants, photocatalytic oxidation, etc. Despite the availability of the above-mentioned processes for the removal of organic pollutants, the adsorption process still remains the best because of its simple design and easy operation. Although microbial degradation and chemical oxidation methods can be employed for the removal of nitrophenol, drawbacks like slow reaction rates, disposal of sludges, and control of temperature and pH are associated with microbial degradation, while chemical oxidation is only economically feasible at high pollutant concentrations.[2,6]

Adsorption technology is currently being used extensively for the removal of organic and inorganic micropollutants from the aqueous phase, and activated carbon has been the water industry's standard adsorbent for reclamation of municipal and industrial wastewater. Activated carbons are the most widely used adsorbents for the removal of pollutants from wastewater due to their extended surface area, microporous structure, high adsorption capacity, and high degree of surface reactivity. Extensive research work has been carried out using activated carbons and resins.[7,8] Despite the prolific use of these adsorbents in wastewater treatment, carbon adsorption remains an expensive treatment process. This has prompted a growing research interest in the production of low-cost alternatives to activated carbon. Some adsorbents that were developed from low-cost materials include fertilizer waste,[9] wood,[10] and rice husk,[11] activated jute stick char[12] by several chemical treatments. The use of sawdust for the removal of phenol from aqueous solution has been studied by Sivanandam and Anirudhan.[13] Dutta et al.[14] carried out studies on adsorption of *p*-nitrophenol on charred saw dust. Ahmaruzzaman and Sharma[15] investigated the possible use of coal, residual coal, rice husk, and petroleum coke as a means of removal of *p*-NP from wastewater.

A study on tea waste as a low-cost adsorbent for *p*-NP removal is of interest because of its good removal capacity and also considering the fact that India is the second largest producer of tea (*Camellia sinensis*) in the world, with the state of Assam alone being a vast producer and consumer of tea. A huge amount of tea waste is being produced from a number of tea industries during the processing of tea leaves, and their disposal is another solid waste disposal problem. Considering the large scale availability of tea waste of *Camellia assamica* and *Camellia sinensis* in this region, research work on utilization of the tea waste for *p*-NP removal will help to some extent in solving this problem besides providing a cost-effective adsorbent requiring no regeneration. Adsorbents of agricultural/lignocellulosic precursors often show the presence of functional groups

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10.1021/je100117s

like −COOH, −OH, etc. The presence of structural hydroxyl protons, carboxylic protons, and lactone protons in tea waste is responsible for its ion-exchange behavior. Phenol and substituted phenol, in general, contain one or more of the following functional groups in their structure: −OH, $-NO_2$, Cl, NH_2, and CH_3, etc. It is believed that the interaction of the above functional groups with the adsorbent material being used could be from covalent to Coulombic, hydrogen bonding, or weak van der Waals forces. The ability of the phenols to be eluted out depends on the strength and type of interaction. Because of the presence of structural hydroxyl and carboxylic groups, it is expected that phenols could be bound either by hydrogen bonds or by weak van der Waals forces.

Earlier investigations on tea leaves were carried out for the treatment of Cr(VI) containing wastewater.[16−18] Tea wastes have also been employed for the removal of organic pollutants of dye categories, such as methylene blue,[19] basic dyes,[20] etc., from wastewater. However, to the best of our knowledge, tea waste has never been utilized for the removal of phenolic compounds from wastewater. We have, therefore, made use of this abundantly available tea waste through activation by means of phosphoric acid treatment to increase the surface area and porosity of activated tea waste and hence its adsorption capacity for the adsorption of *p*-NP. The objective of this study was to investigate the possibility of using activated tea waste (ATW) as an adsorbent material in *p*-NP adsorption.

Experimental Section

Materials. All the reagents used for experimental studies were of analytical grade. The adsorbate used was *p*-nitrophenol (*p*-NP), and the activating chemical, orthophosphoric acid, was of AR grade. The adsorbent, viz., tea waste, was obtained from the local tea industry. Sodium hydroxide, hydrochloric acid, sodium bicarbonate, sodium carbonate, sodium chloride, sodium sulfate, and sodium nitrate used were obtained from Merck India Ltd. The solutions of *p*-NP were prepared in deionized water.

Preparation of Adsorbent. Tea waste was obtained from the local tea estates of Assam. Prior to phosphoric acid treatment, tea waste was repeatedly boiled and washed with distilled water to remove soluble and color components until the water was virtually colorless. This effort was done to avoid possible interference of the soluble portion or color components in absorbance readings on the UV−visible spectrophotometer. It was then rinsed with distilled water and dried in an oven at 65 °C for 5 h. A sufficient amount of orthophosphoric acid was then added to the pretreated tea waste and stirred vigorously by maintaining at 100 °C for 2 h and activated at 500 °C in a muffle furnace for 2 h under a nitrogen atmosphere at a constant heating rate of $10\ °C \cdot min^{-1}$. Finally, it was washed with distilled water repeatedly until it became neutral and dried in an oven at a temperature of (105 to 110) °C for 12 h to remove all the volatile components and was kept in desiccator until use. The adsorbent was finely ground for use in adsorption. It has been shown that lignocellulosic materials are favored for activation by chemical processes,[21] especially using H_3PO_4 as the chemical reagent, and since the proven composition of tea waste has a cellulosic component, H_3PO_4 has been used as the activating agent. The evolution of tarry substances during carbonization by a physical method is also avoided through chemical activation by H_3PO_4.

Effect of Different Activating Agents. The influence of different activating agents, viz., H_3PO_4, $ZnCl_2$, KOH, H_2O_2, NaOH, and MnO_2, on tea waste was studied to choose the best activating agent on the basis of adsorption capacity. These chemical reagents promote the formation of cross links, leading to the formation of a rigid matrix less prone to volatile loss and volume contraction upon carbonization.[22−24] Besides an increase in the porous structure, carbon burn-off is not required in chemical treatment. The method of preparation of the adsorbent was the same as adopted for ATW except that the activating agent is different in this case. Equal weights (0.2 g) of activated tea wastes prepared from different chemical reagents were kept until equilibration at 25 °C, and supernatant solutions were analyzed for residual *p*-NP concentration.

Batch Adsorption. The effect of different controlling parameters like pH, contact time, and anions on *p*-NP adsorption by activated tea waste was studied using batch adsorption experiments. Batch experiments were conducted by contacting known amounts of the adsorbent with 20 mL of synthetic wastewater containing $1000\ mg \cdot L^{-1}$ of aqueous *p*-NP solution. The method involved agitating different amounts of the adsorbent [(0.2 to 2) g] with 20 mL of $1000\ mg \cdot L^{-1}$ of *p*-NP aqueous solution. All the batch experiments were carried out at their optimum pH. The solution containing the adsorbent was left for 24 h. The supernatant solution was then analyzed for residual concentration of *p*-nitrophenol at $\lambda_{max} = 315$ nm using a Cary Bio UV−visible spectrophotometer (Varian Company). To reduce the measurement errors, the UV absorption intensity of each sample was measured in triplicate, and the average value was used to calculate the equilibrium concentration based on the standard calibration curve within R^2 (coefficient of determination) of 0.99.

For pH studies, fixed amounts of the adsorbents were taken in several conical flasks containing 20 mL of aqueous *p*-NP and pH before adsorption was adjusted using 0.1 M HCl and 0.1 M NaOH with the help of a sensIon 3 Laboratory pH meter (Hatch Company). The amount of adsorption of *p*-NP was again analyzed using UV spectrophotometry. The pH during the course of adsorption was also studied.

In all the above analyses, the measurement of equilibrium adsorption, q_e, or x/m was calculated as per eq 1

$$q_e = \frac{(C_o - C_e) \cdot V}{m \cdot 1000} \tag{1}$$

where q_e is the adsorption capacity in $mg \cdot g^{-1}$; C_o and C_e are the initial and equilibrium concentrations of the solute ($mg \cdot L^{-1}$); V is the volume of *p*-NP solution (mL); and m is the mass of the adsorbent (g). The Freundlich, Langmuir, Temkin, Dubunin−Radushkevich, and Redlich−Peterson adsorption models have been used to describe the equilibrium nature of the adsorption of *p*-NP in the present study.

Kinetic Studies. The equilibrium adsorption time for the uptake of *p*-NP by activated tea waste was estimated through kinetic studies. Fixed amounts of the adsorbents were taken in several glass stoppered conical flasks containing $1000\ mg \cdot L^{-1}$ of aqueous *p*-NP (20 mL), and the solution containing the adsorbent was left for different time intervals by shaking at a controlled speed of 150 rpm for different adsorption times. At the end of the predetermined time *t*, the flasks were withdrawn and their contents filtered, and the residual *p*-NP concentration in the filtrate was determined. The amount of *p*-NP adsorbed onto filter paper during the filtration was less than 1 %, and hence the effect of filter paper on the adsorption of the adsorbent has been neglected during the studies. The adsorption kinetics was followed for 24 h. The kinetics of adsorption of *p*-NP was investigated using various kinetic models, pseudo-first-order, pseudo-second-order, and intraparticle diffusion models.

Adsorption Isotherm. The experimental adsorption data were analyzed using the Langmuir, Freundlich, Dubunin−Radushkevich, Temkin, and three-parameter Redlich–Peterson linearization models to determine the best model that characterizes the adsorption mechanism. Figure 4 shows the adsorption isotherm of phosphoric acid treated tea waste along with its validation with the above-mentioned isotherms. The Langmuir model is based on monolayer, uniform, and finite adsorption site assumptions. The Langmuir equation can be expressed as

$$\frac{C_e}{q_e} = \frac{1}{ab} + \frac{C_e}{a} \tag{2}$$

where C_e = equilibrium concentration of the adsorbate in solution after adsorption ($\text{mg}\cdot\text{L}^{-1}$); q_e = amount adsorbed per unit weight of adsorbent ($\text{mg}\cdot\text{g}^{-1}$); and a and b are Langmuir constants. The value of a ($\text{mg}\cdot\text{g}^{-1}$) and b ($\text{L}\cdot\text{mg}^{-1}$) can be determined from the slope and intercept of a linear plot of C_e/q_e versus C_e.

The Freundlich model is an empirical equation for multilayer, heterogeneous adsorption. The linearized form of the Freundlich equation is

$$\log q_e = \log k_F + 1/n \log C_e \tag{3}$$

where k_F is the Freundlich equilibrium constant which is an indication of adsorption capacity and $1/n$ is an empirical constant related to the efficiency of adsorption: if $1/n > 1$, the adsorption is unfavorable, while if $1/n < 1$, the adsorption is favorable.

The Temkin equation is based on the assumption that the heat of adsorption would decrease linearly with an increase in coverage of the adsorbent and is given as

$$q_e = B \ln k_T - B \ln C_e \tag{4}$$

where $B = ((RT)/b_T)$; b_T is the constant related to the heat of adsorption; k_T is the Temkin isotherm constant; R is the gas constant; and T is the absolute temperature in Kelvin.

The Dubunin–Radushkevich isotherm assumes that there is a variable adsorption potential where the free energy of adsorption is related to the degree of pore filling and is expressed mathematically as

$$\ln q_e = \ln q_{DR} - \left(\frac{RT}{E}\right)^2 \left(\ln \frac{C_o}{C_e}\right)^2 \tag{5}$$

where q_{DR} is the Dubunin–Radushkevich constant representing the theoretical monolayer saturation capacity and E is the mean sorption energy which may provide useful information whether the adsorption is subject to a physical or chemical process.

The Redlich–Peterson isotherm is a three-parameter model which compromises the features of the Langmuir as well as Freundlich isotherm and whose equation is given as

$$\ln\left[K_R \frac{C_e}{q_e} - 1\right] = \ln a_R - \beta \ln C_e \tag{6}$$

where K_R and a_R are the Redlich–Peterson constants and β is basically in the range of zero to one.

Procedure for Determination of pH$_{ZPC}$ of ATW. The pH at which the charge on the surface of activated tea waste is zero is referred to as the pH$_{ZPC}$. An amount of 50 mL of 0.01 M NaCl solutions was prepared and added into a series of Erlenmeyer flasks. Then the pH values were adjusted in the range between 1 and 12 using 0.01 M HCl and 0.01 M NaOH. The initial pH of the solutions was measured with a pH meter and noted as pH$_{\text{initial}}$. After a constant value of pH$_{\text{initial}}$ had been reached, 0.15 g of activated sample was added into each Erlenmeyer flask. The solution pH was measured after 48 h and noted as pH$_{\text{final}}$, then plotted against pH$_{\text{initial}}$. The pH$_{ZPC}$ of activated tea waste is the point when pH$_{\text{initial}}$ = pH$_{\text{final.}}$

Table 1. Carbon Surface Functionalities on Activated Tea Waste (Boehm Titration)

	n_{CSF} ($\mu\text{mol}\cdot\text{g}^{-1}$)
(a) acidic groups	
(1) phenolic	2.407
(2) lactonic	1.612
(3) carboxylic	3.073
(b) basic groups	1.389

Analysis of Activated Tea Waste. The physical and chemical analysis of ATW was conducted according to an American Standard Testing Method (ASTM). Proximate analysis of the adsorbent constituted determination of moisture content, volatile matter, fixed carbon, and ash content. Ultimate analyses include determination of carbon, hydrogen, and nitrogen content. The Boehm titration has been used extensively as a chemical method for identifying oxygen surface groups of various adsorbents.[25,26] The titration procedure was performed according to the standardized method[27] where 1.5 g of the adsorbent was added to 50 mL of each of the three reaction bases, viz., 0.05 M $NaHCO_3$, Na_2CO_3, and NaOH solutions. The samples were agitated by shaking for 24 h and filtered. An amount of 10 mL of the filtrate aliquots of $NaHCO_3$ reaction base was then acidified with 20 mL of 0.05 M HCl, while the aliquots of the reaction base Na_2CO_3 were acidified with 30 mL of 0.05 M HCl. The acidified solutions were then back-titrated with 0.05 M NaOH, the titrator base. The aliquots of NaOH reaction base were titrated using two different methods: (1) the solution was acidified by the addition of 20 mL of 0.05 M HCl and the sample back-titrated with 0.05 M NaOH and (2) the solution was directly titrated with 0.05 M HCl.

In all the above titrations, CO_2 was removed from the solutions immediately before titration by passing Ar gas for 2 h maintained at a pressure of 0.5 $\text{kg}\cdot\text{cm}^{-2}$ using capillary tubes submerged in the solution to be titrated. A pH electrode was used for the end point determination where the titration was carried out until a pH of 7.0 was measured. NaOH used in the experiment was in the form of pellets whose solution was standardized using dried and desiccated potassium hydrogen phthalate. This standardized NaOH was then used for standardization of the HCl solution.

The amounts of acidic groups on the ATW surface were determined by the equation below

$$n_{CSF} = \frac{n_{HCl}}{n_B}[B]V_B - ([HCl]V_{HCl} - [NaOH]V_{NaOH})\frac{V_B}{V_a} \tag{7}$$

The amount of basic groups was determined with the help of the following equation

$$n_{CSF} = [B]V_B - ([HCl]V_{HCl})\frac{V_B}{V_a} \tag{8}$$

where [B] and V_B are the concentration and volume of the reaction base; n_{CSF} refers to the moles of carbon surface functionalities on the surface of the carbon that reacted with the base during the mixing step; V_a is the volume of the aliquot taken from V_b; and [HCl] and V_{HCl} are the concentration and volume of the acid added to the aliquot. Table 1 shows the different surface functionalities of ATW.

Column Studies. Fixed bed studies were conducted in a fixed bed of down-flow 20 mm diameter glass columns. The treated

Table 2. Physical and Chemical Characteristics of Activated Tea Waste

ultimate (wt %, dry ash-free basis)		proximate (wt %, as received)	
carbon	47.11	moisture	0.60
nitrogen	5.22	volatile matter	40.00
hydrogen	2.0	fixed carbon	57.1
		ash content	2.29

typical properties	
loss on ignition	86 %
particle size	300 μm
pH_{ZPC}	2.4
surface area (BET)	29.5 $m^2 \cdot g^{-1}$
bulk density	0.36 $g \cdot cm^{-3}$
pore size	2.1 nm

solution was collected from the bottom of the column and analyzed for residual concentration of *p*-nitrophenol. The flow rate was kept at 30 $mL \cdot h^{-1}$.

Quality Assurance. All the experiments were repeated thrice, and average values obtained are being reported. The experimental blanks were also run in parallel to establish accuracy, reliability, and reproducibility. All glassware and other apparatuses used in the study were presoaked in a 10 % HNO_3 solution for 1 day, rinsed with deionized water, and dried in an oven.

Results and Discussion

Characterization of Activated Tea Waste. Results of proximate, ultimate, and other physical and chemical characteristics are given in Table 2. The ATW showed low moisture and ash content which appeared to be a very suitable material for use in the adsorption process. The fixed carbon content was comparatively high and found to be 57.1 %.

A leaching test was performed on activated tea waste by scanning the filtrate of ATW placed in 20 mL of deionized water by UV−visible spectrophotometry for the presence of any peaks that may interfere in the absorbance readings. The absence of notable peaks showed the absence of soluble fraction in ATW which has therefore no role in the entire study performed.

FTIR Study of the Adsorbent. The adsorption mechanism of *p*-NP on ATW can be better understood from a FTIR study of ATW before and after adsorption. The *p*-NP loaded adsorbent was air-dried at room temperature and stored in a desiccator before being used for preparation of KBr pellets for IR analysis of the adsorbent after adsorption of *p*-NP. The adsorbent sample before adsorption was also prepared by the KBr pellet method for IR study. The infrared (IR) spectrum of the adsorbent and *p*-NP loaded adsorbent is shown in Figures 1 and 2, respectively. The complex nature of the adsorbent is displayed by the number of adsorption peaks in the spectra. The recorded FTIR spectra of ATW before adsorption showed a sharp bend at 3429.4 cm^{-1} due to asymmetric stretching of the N−H group confirming the existence of an amino group. The peak at 3333.0 cm^{-1} is due to OH stretching of the COOH group, while the peak at 2970.4 cm^{-1} is likely due to the C−H normal mode. The OH stretching of the COOH group is responsible for the band near 2630 cm^{-1}. The spectrum also showed a strong peak at 2904.8 cm^{-1} due to the C−H group. A broad peak near 1726 cm^{-1} may be due to a carbonyl ester group. A sharp peak at 1959.7 cm^{-1} is due to a hydroxyl group, while the peak generated at 1612 cm^{-1} is due to the aromatic ring vibration. The peak at 1502 cm^{-1} is due to C═C symmetric stretching of double bonds, while the peaks between (700 and 1000) cm^{-1} are due to ═C−H bending of alkenes.

The FTIR spectrum of ATW after adsorption also showed characteristic peaks at (3429.4, 3333.0, 2970.4, and 2904.8) cm^{-1} which are similar to the peaks observed in ATW before adsorption. The peaks at 2630.9 cm^{-1} were shifted to 2629.0 cm^{-1}, 1959.7 cm^{-1} to 1955.8 cm^{-1}, 1612.5 cm^{-1} to 1610.6 cm^{-1}, and 1014.6 cm^{-1} to 1012.6 cm^{-1}. Due to the adsorption of *p*-NP on the surface of ATW, some prominent peaks due to H-bonded −O−H stretch of the phenolic group are observed at (3294.4, 3250.1, and 3209.6) cm^{-1}. The peaks at 1527.6 cm^{-1} and 1508.3 cm^{-1} are due to N═O stretching, while that at 1460.1 cm^{-1} is due to N═O bending of the nitro group. The presence of these bands confirmed the adsorption of *p*-NP. FTIR analysis of the two spectra showed that the H-bonded O−H stretch, C−C═C symmetric stretch, and C−O stretch of esters may be held responsible for the adsorption of *p*-NP on the ATW surface.

Effect of Different Activating Agents. The difference in the nature of chemical reagents affects the porosity development of the carbon derived from tea waste. Comparative adsorption data were obtained for the char, NaOH, $ZnCl_2$, KOH, H_3PO_4, H_2O_2, and MnO_2 treated tea waste as (26.73, 39.18, 78.63, 77.28, 94.60, 28.42, and 8.19) $mg \cdot g^{-1}$, respectively. The result showed that H_3PO_4 was the best activating agent for tea waste for the adsorption of *p*-NP from aqueous solution. Hence, in the present study, H_3PO_4 activated tea waste (ATW) was used as the adsorbent for the removal *p*-NP from aqueous solution.

Determination of pH_{ZPC} of ATW. The carbon surface charge is mainly determined by the pH of the adsorbate solution. It is known[28] that the net charge on the carbon surface is positive at a solution pH lower than that corresponding to the point of zero charge (pH_{ZPC}) of the surface and is negative at a solution pH higher than pH_{ZPC}. Therefore, it is very important to determine the pH_{ZPC} for the carbon material. The pH_{ZPC} is the pH when the charge on the activated carbon surface is zero. The pH_{ZPC} of ATW was determined to be 2.4 (Figure 3).

Adsorption Isotherms. The analysis and fitting of isotherm data to different isotherm models is a vital step in determining a suitable model that can be used to describe the adsorption process. The linear regression line obtained from the Langmuir equation had a highly significant R^2 value (0.995) indicating a good fit to this model, whereas the low R^2 value (0.964) from the Freundlich isotherm showed poor agreement with the data. The Langmuir constants "a" and "b" can be determined from the slope and the intercept of the plot of C_e/q_e versus C_e. The value of a corresponds to the theoretical monolayer saturation capacity of the adsorbate on the adsorbent, and b is related to the adsorption energy. The Temkin isotherm showed moderate fitting with the equilibrium data ($R^2 = 0.981$). The value of B and k_T was evaluated from the linear plot of q_e versus ln C_e. The Redlich−Peterson and Dubunin−Radushkevich models showed comparatively low fitting with R^2 values of 0.973 and 0.979, respectively. Figure 4 shows the comparison of the experimental adsorption isotherms with that obtained from the Freundlich, Langmuir, Tempkin, Dubunin−Radushkevich, and Redlich−Peterson isotherms. On the basis of the coefficient of determination (R^2 value), i.e., the isotherm giving R^2 value closest to unity, the fitting is Langmuir > Temkin > Dubunin−Radushkevich > Redlich−Peterson > Freundlich. The adsorption constants for various isotherms are reported in Table 3.

The adsorption capacity thus determined from the Langmuir isotherm was 142.85 $mg \cdot g^{-1}$ for the activated tea waste. The essential characteristics of the Langmuir isotherm have been described by the equilibrium constant, R_L, which is defined as $R_L = 1/(1 + bC_o)$, where C_o is the initial concentration of the

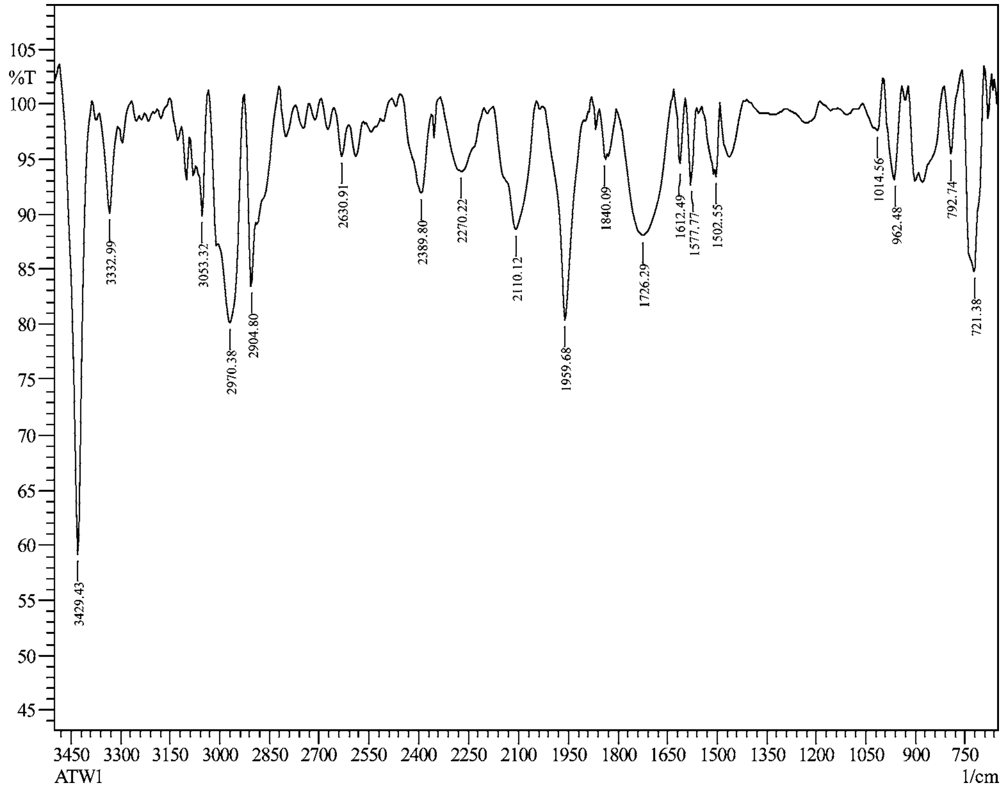

Figure 1. FTIR spectra of ATW before adsorption of *p*-NP.

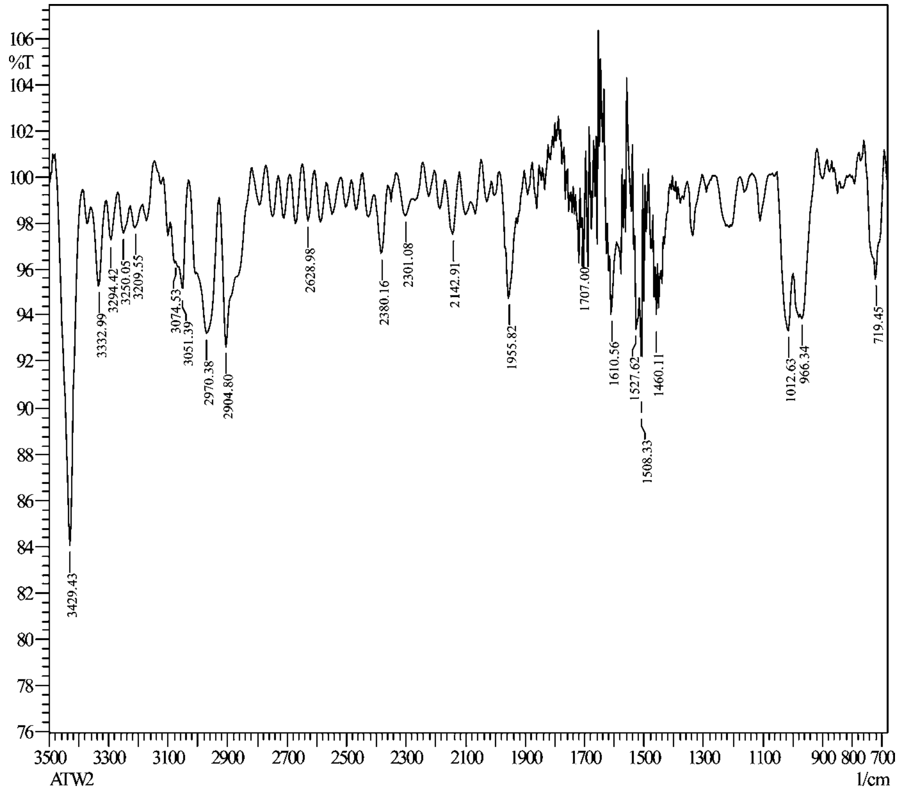

Figure 2. FTIR spectra of ATW after adsorption of *p*-NP.

adsorbate *p*-NP and *b* is the Langmuir constant. This indicates the nature of the adsorption[11] as

$$0 < R_L < 1, \text{ favorable; } R_L > 1, \text{ unfavorable; } R_L = 0, \text{ irreversible; } R_L = 1, \text{ linear}$$

The value of R_L in the present investigation has been found to be $2.27 \cdot 10^{-6}$, i.e., below 1 for *p*-NP at $T = 25$ °C, showing that the adsorption of *p*-NP is very favorable. The value of R_L being very close to the lower acceptable range (close to zero) indicates a high degree of irreversibility of the process.

Effect of pH. It is clear from Figure 5 that the extent of adsorption is higher in acidic solution than in basic solution. The % adsorption of *p*-NP decreases with an increase in alkalinity of the medium. The adsorption of *p*-NP by the ATW

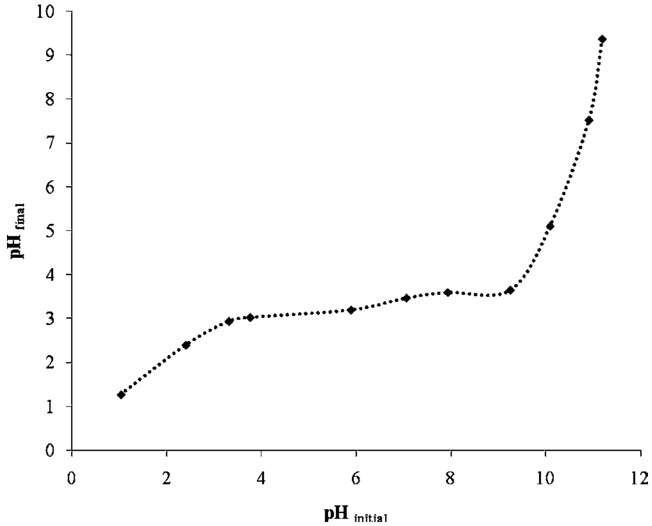

Figure 3. Determination of pH_{ZPC} of ATW at 25 °C.

Table 3. Isotherm Parameters for Adsorption of *p*-Nitrophenol on Activated Tea Waste

isotherm	parameters			R^2
Langmuir	a ($mg \cdot g^{-1}$)	B ($m \cdot g^{-1}$)		
	142.85	0.021		0.995
Freundlich	K_F ($mg \cdot g^{-1}$)	$1/n$		
	2.96	0.47		0.964
Temkin	K_{Tem} ($L \cdot g^{-1}$)	B ($J \cdot mol^{-1}$)		
	0.293	25.81		0.981
Dubunin−Radushkevich	q_{DR}	E ($kJ \cdot mol^{-1}$)		
	129.02	9.10		0.979
Redlich−Peterson	n	β	q_m ($mg \cdot g^{-1}$)	
	0.859	0.60	11.46	0.973

surface was nearly equal in the pH range 2 to 7.12, and thereafter it drops suddenly which decreases gradually with an increase in pH of the solution. It may be linked[12] with the fact that the pK_a of *p*-NP is 7.18. At low solution pH, the adsorption affinity of ATW toward *p*-NP is high. This is due to the existence of *p*-NP in molecular form at low pH conditions. At a pH greater than the pH_{ZPC} of ATW, the surface of the adsorbent is negatively charged, and above the pK_a of the solute, *p*-NP exists mainly in the ionic form. As the solution pH increases, the concentration of the anionic form of *p*-NP and negative charge of ATW increases which results in high electrostatic repulsion between the solute molecules[29] and between the solute and ATW surface owing to which the adsorption of *p*-NP is mainly due to the molecular form of the solute. Hence the % adsorption of *p*-NP at higher pH is low as depicted in Figure 5. A maximum adsorption of 95.44 % was observed at a pH around 2.4 which was equal to that of the pH_{ZPC} of ATW (Table 2) as the net charge on the surface of ATW was nearly zero and there was no electrostatic repulsion.

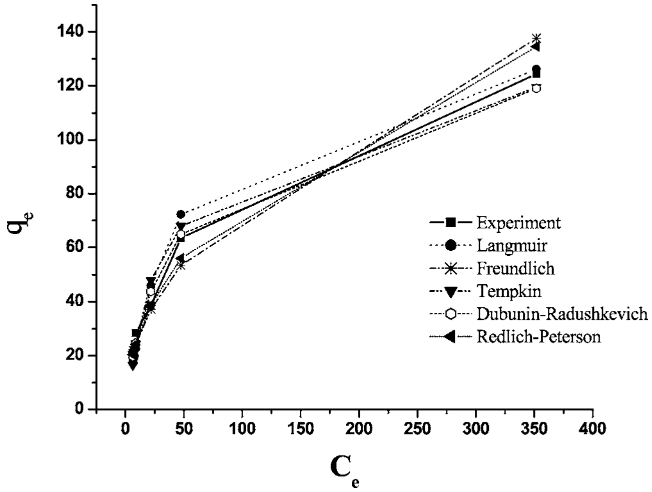

Figure 4. Validation of the adsorption isotherm for *p*-NP removal (temperature, 25 °C; C_o, 1000 $mg \cdot L^{-1}$ of *p*-NP).

Effect of Ionic Strength. Wastewater contains apart from pollutants different salts at different levels of concentration, and it was therefore worthy to study the effects of various anions like chloride, sulfate, and nitrate on adsorption. Their influence on *p*-NP adsorption was studied by varying the amounts of chloride, sulfate, and nitrate solutions, and the data obtained are given in Table 4. From Figure 6, it was found that the presence of these anions has some effect on the adsorption of *p*-NP. The percentage removal was the lowest in the presence of the chloride ion. With a gradual increase in concentration, a drop in percent removal was achieved in each case. At higher anion concentrations (above 0.5 M), there is no adverse effect on *p*-NP adsorption onto ATW. The minimum percent removal in the presence of sodium chloride, sodium sulfate, and sodium nitrate was 69.3 %, 77.34 %, and 76.56 %, whereas in the absence of the anions the percentage removal was nearly 85.8 %. The adsorption capacity in the presence of these ions might also block the active sites of the adsorbent surface thus reducing the capacity of *p*-NP adsorption by ATW. On the whole, it was found that the adsorption yield was decreased in the presence of these anions.

Effect of Contact Time on Adsorption. The amount of *p*-NP adsorbed increases with contact time and attains equilibrium at about 5 h for activated tea waste (Figure 7). The uptake of adsorbate species was fast in the initial stages of the contact period, and thereafter it became slower near the equilibrium. In the initial stage, there exists increased concentration gradients between the adsorbate molecules in the solution and the adsorbates on the adsorbent surface. Due to this driving force of concentration gradient, *p*-NP adsorption is high during the initial stages. After some lapse of time, this concentration is reduced due to the accumulation of *p*-NP on the ATW surface, and the adsorption reaches its equilibrium where the adsorption rate equals the desorption rate after which the rate of *p*-NP uptake remains almost asymptotic with time.

Kinetics of the Adsorption Process. The kinetic data of *p*-NP removal onto activated tea waste (ATW) were analyzed using a pseudo-first-order equation [eq 9] and pseudo-second-order model [eq 10]. The pseudo-first-order equation[30−32] is

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \tag{9}$$

A plot of $\log(q_e - q_t)$ against t should give a linear relationship with the slope of $(k_1/2.303)$ and intercept of $\log q_e$.

The pseudo-second-order equation[31−33] is expressed in the form

$$\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e} \tag{10}$$

where q_e is the adsorption capacity at equilibrium ($mg \cdot g^{-1}$); q_t is the adsorption capacity at time t ($mg \cdot g^{-1}$); k_1 is the rate constant of the pseudo-first-order equation (min^{-1}); and k_2 is the second-order rate constant of sorption ($g \cdot mg^{-1} \cdot min^{-1}$).

If the pseudo-second-order kinetic equation is applicable, a plot of t/q_t against t [eq 10] should give a linear relationship. The q_e and k_2 can be determined from the slope and intercept of the linear plot given by eq 10. The pseudo-first-order rate

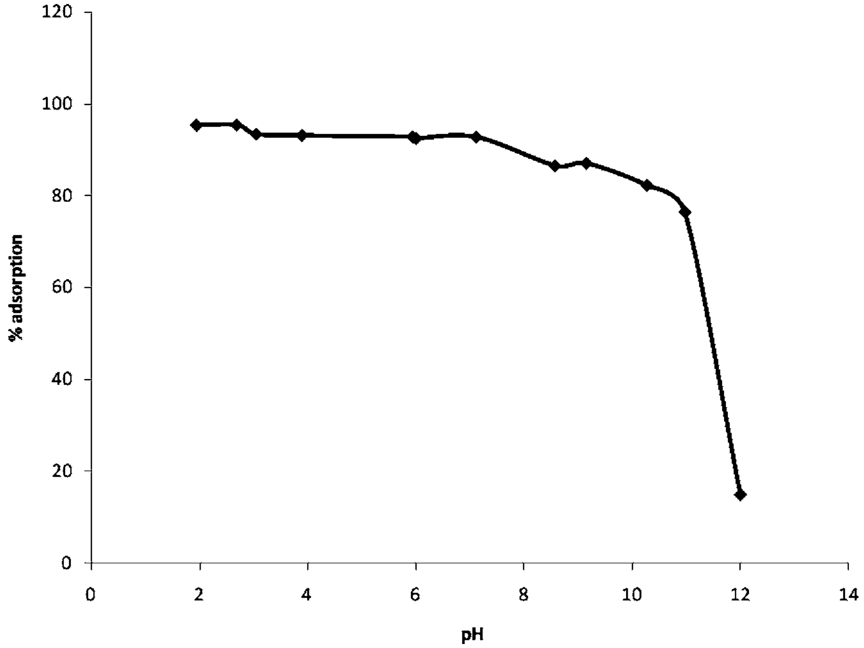

Figure 5. Effect of solution pH on the adsorption of *p*-NP (temperature, 25 °C; $C_o = 1000\ \mathrm{mg \cdot L^{-1}}$).

Table 4. Effect of Ionic Strength on Adsorption of *p*-Nitrophenol by Phosphoric Acid Activated Tea Waste

	% removal of *p*-NP		
anion concentration (M)	chloride	sulfate	nitrate
0	85.8	85.8	85.8
0.01	77.7	84.06	83.07
0.1	80.1	84.21	76.56
0.3	69.3	77.34	76.65
0.5	80.1	77.88	85.38
1	74.79	75.81	84.03

constant k_1, the amount of *p*-nitrophenol adsorbed at equilibrium, and the coefficient of determination are shown in Table 5. The pseudo-second-order constant k_2, amount of phenol adsorbed at equilibrium q_e, and the corresponding coefficient of determination values are also reported in Table 5. From Table 5, it was noticed that the R^2 values were found to be higher for the pseudo-second-order compared to that of the pseudo-first-order kinetic model. In the view of these results, it can be said that the pseudo-second-order kinetic model provided a good correlation for the adsorption of *p*-nitrophenol onto ATW in contrast to the pseudo-first-order model. It can be concluded that adsorption of *p*-NP onto ATW follows pseudo-second-order kinetics. It indicates that physical interaction is involved in the adsorption process, which may be partly due to H-bonding between the hydroxyl group of *p*-NP and some active functional groups in the ATW. Similar results were also obtained for the adsorption of *p*-nitrophenol on activated carbon fiber.[34]

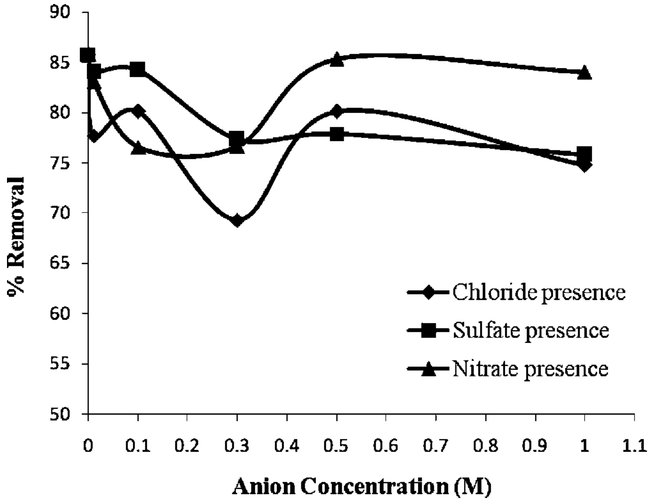

Figure 6. Effect of different anion concentration on adsorption of *p*-NP on ATW (temperature, 25 °C; anion dose, 0.2 g).

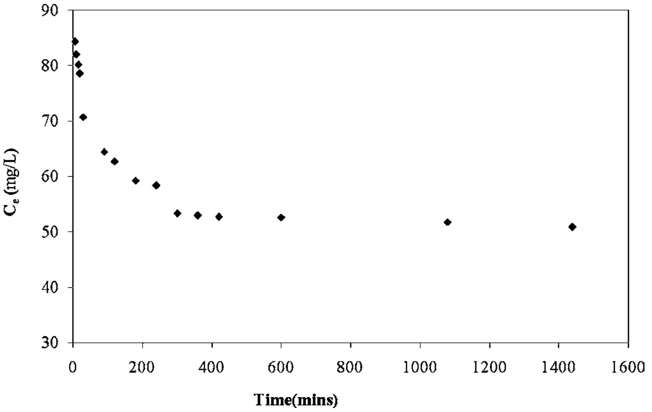

Figure 7. Effect of contact time on the removal of *p*-NP.

Adsorption Mechanism. The adsorption behavior, i.e., the adsorbate transport from the solution phase to the surface of the adsorbent particles, occurs in several steps. It may be controlled either by one or more steps, e.g., external diffusion, pore diffusion, surface diffusion, and adsorption on the pore surface, or by a combination of more than one step. A plot of q_e, the amount of adsorbate adsorbed per unit weight of the adsorbent, versus the square root of time has been commonly used to describe whether the adsorption process is controlled by an intraparticle diffusion model.[30]

If a Weber–Morris plot[31] of q_t versus $t^{0.5}$ gives a straight line, then the sorption process is controlled by intraparticle diffusion only. However, the data exhibit a multilinear plot, indicating that more than one step influences the sorption process (Figure 8).

The shape of the Weber–Morris plot reveals that the adsorption of *p*-NP onto activated tea waste is controlled by

Table 5. Kinetic Parameters for the Adsorption of *p*-NP of Activated Tea Waste

		pseudo-first-order				pseudo-second-order	
C_o (mg·g^{-1})	q_e(exptl) (mg·g^{-1})	k_1·10^{-3} (min^{-1})	q_e(calcd) (mg·g^{-1})	R^2	k_2·10^{-2} (g·mg^{-1}·min^{-1})	q_e(calcd) (mg·g^{-1})	R^2
1000	142.85	6.90	2.77	0.947	1	100	1

external mass transfer followed by a gradual adsorption stage with intraparticle diffusion dominating. The shape of the Weber−Morris plot can be very helpful in depicting the process going on during the entire adsorption. The first sharp portion indicates external surface adsorption, while the second curved portion is the gradual adsorption stage, where intraparticle diffusion is the rate-limiting step and the final linear portion is the equilibrium stage where adsorption slows down due to an extremely low solute concentration. The pore diffusion coefficient, *D*, for the removal of *p*-NP has been calculated using eq 11, assuming spherical shape geometry for the adsorbent.[31,32]

$$t_{1/2} = 0.03 r_o^{\,2}/D \tag{11}$$

where $t_{1/2}$ is the time for the half adsorption; r_o is the diameter of the adsorbent particles, i.e., $18 \cdot 10^{-4}$ cm; and *D* is the pore diffusion constant, cm^2·s^{-1}. The value of the pore diffusion coefficient of *p*-NP was found to be $5.4 \cdot 10^{-5}$ cm^2·s^{-1} indicating pore diffusion is not significant.[33,35] The transport number to know the mode of diffusion was computed from eq[36,37] 12

$$\log \frac{Q_t}{Q_\infty} = \log k + n \log t \tag{12}$$

where Q_∞ = weight of the adsorbate with adsorbent at equilibrium; k = adsorbate−adsorbent interaction coefficient; n = transport number; and t = time. The slope of the plot of log Q_t/Q_∞ against log *t* was used to calculate the transport number, *n*, which was found to be 0.007. Figure 9 shows the plot of log Q_t/Q_∞ versus log *t*. The value of *k* was evaluated from the intercept of the plot.

The value of *n* indicates the type of transport mechanism. A value of $n = 0.5$ represents a Fickian mechanism, while $n = 1$ indicates a non-Fickian mechanism. As the value of *n* is less than 0.5, it indicates a Fickian mechanism of diffusion of *p*-NP onto ATW.

Column Studies. Column-type continuous flow operations appear to have a distinct advantage over batch-type operations because the rate of adsorption depends on the concentration of solute in the solution being treated. For column operation, the adsorbents are continuously in contact with a fresh solution. Consequently, the concentration in the solution in contact with a given layer of adsorbent in a column is relatively constant. For batch treatment, the concentration of solute in contact with a specific quantity of adsorbent steadily decreases as adsorption proceeds, thereby decreasing the effectiveness of the adsorbent for removing the solute. The breakthrough capacity, which is the amount adsorbed before the appearance of adsorbates in the effluent, and the total capacity, which is the amount adsorbed until the effluent concentration of the adsorbate is equal to the influent solution concentration, are computed from breakthrough curves. The results of the column studies plotted in Figure 10 reveal that up to 50 min there is no trace of *p*-nitrophenol in the effluent when ATW is used as adsorbent. The adsorption capacity of the adsorbent was exhausted after 360 min of column operation. Thus, the breakthrough time for *p*-nitrophenol by using ATW was found to be 50 min. The performance of the column bed is usually described through the concept of a breakthrough curve, which is obtained by plotting throughput

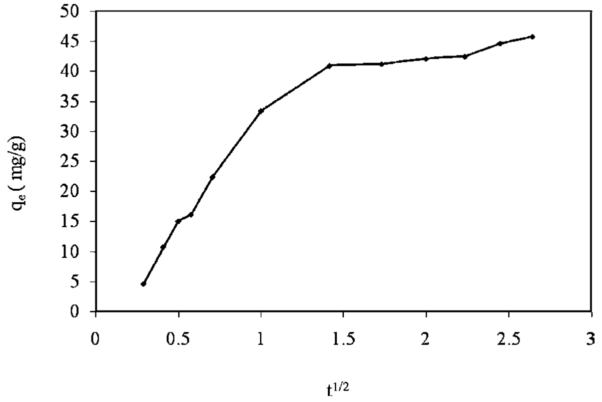

Figure 8. Weber−Morris plot for intraparticle diffusion (temperature, 25 °C; C_o, 1000 mg·L^{-1}; adsorbent dose = 10 g·L^{-1}).

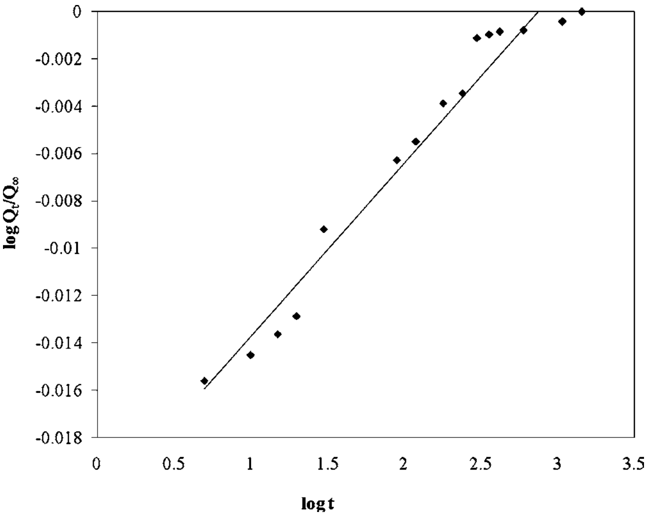

Figure 9. Kinetics of mass transfer.

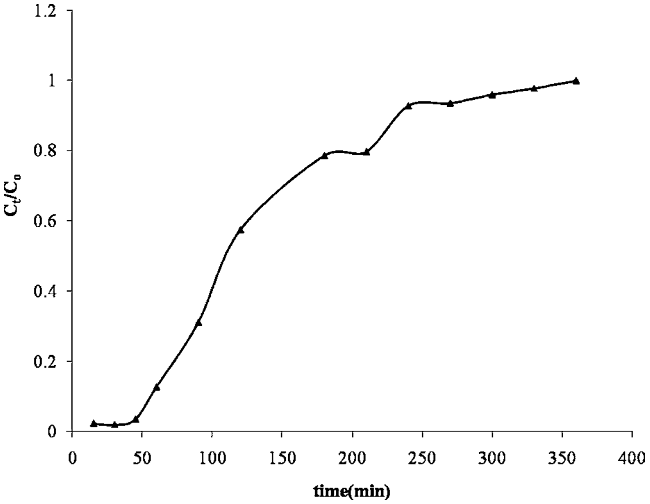

Figure 10. Breakthrough curve for ATW (temperature, 25 °C; flow rate, 2 mL·min^{-1}; C_o, 1000 mg·L^{-1}).

volume (V_t) at any time (t) versus effluent *p*-NP concentration (C) as shown in Figure 10. Throughput volume was calculated using eq 13.

$$V_t = Qt \tag{13}$$

where Q is the volumetric flow rate ($\text{mL}\cdot\text{min}^{-1}$). Usually breakthrough is defined as a phenomenon when the concentration from the column is about 3 % to 5 %.[38,39] However, breakthrough at 1 % was also considered and reported on the basis of effluent discharge limits. Exhaustion is usually considered when the effluent concentration remains the same for a long period close to the influent concentration. The area below the breakthrough curve represents the mass of *p*-NP which is not removed (M) and was calculated using eq[40] 14

$$M = \sum\left[\frac{(V_{n+1} - V_n)(C_{n+1} - C_n)}{2}\right] \tag{14}$$

where V_n is the throughput volume at the nth reading (L); V_{n+1} is the throughput volume at the ($n + 1$)th reading (L); C_n the effluent adsorbate concentration at the nth reading ($\text{mg}\cdot\text{L}^{-1}$); and C_{n+1} is the effluent adsorbate concentration at the ($n + 1$)th reading ($\text{mg}\cdot\text{L}^{-1}$). Influent adsorbate load (I) was calculated from throughput volume (V_E) at column exhaustion and influent adsorbate concentration (C_o) according to eq 15.

$$\text{influent adsorbate load (mg)} = I = V_E C_o \tag{15}$$

The mass of adsorbate removed was calculated from difference of influent adsorbate load (I) and mass of adsorbate not removed (M) from eq 16.

$$\text{mass of adsorbate removed} = M_r\ \text{(mg)} = I - M \tag{16}$$

Adsorbate uptake by ATW was calculated using eq 17.

$$\text{adsorbate uptake by ATW, } q_e = \frac{M_r\ \text{(mg)}}{\text{(ATW weight (g))}} \tag{17}$$

The values of M, I, and M_r were evaluated as 586.60 mg, 1500 mg, and 913.39 mg, respectively. The adsorbate uptake from the column study was calculated as 130.48 $\text{mg}\cdot\text{g}^{-1}$.

Costing and Optimization. Cost analysis is an important parameter in determining the criteria for applicability of the adsorbent and selection of the treatment process in industrial use for environmental protection. The cost of the adsorption process is mainly dependent on the cost of the adsorbent used for the removal of the organic compound from wastewater. In developing countries, low-cost materials and their economic feasibility are more important compared to that of commercial activated carbon. The cost for the preparation of the adsorbent is calculated in a stepwise manner (including the physical and chemical activation procedure), thereby calculating the total cost for the preparation of the adsorbent. The cost of commercial activated carbon is Rs.500 per kg in the market. The total cost for preparation of 1 kg of the ATW is Rs.49.84 which includes the cost of the phosphoric acid used, drying, heating, and all overhead costs involved. Since the raw material of the adsorbent is locally available, the cost of transportation is also negligible. This indicates that the cost associated with activated tea waste is much less compared with the commercial activated carbon, and its utilization for the removal of *p*-NP is quite justified.

The comparative data (Table 6) showed that activated tea waste, though not very good as commercial activated carbon, has quite high adsorption capacity for *p*-NP compared to the rest of the adsorbents[41−51] and may be used effectively for the removal of *p*-NP from aqueous streams.

Table 6. Comparison of Adsorption Capacity of Activated Tea Waste with Other Adsorbents

adsorbent	capacity
Activated tea waste (present study)	142.85
Sugar fly ash[41]	0.76−1.15
Wood fly ash[42]	134.9
Fly ash[43]	7.80−9.68
SamLa coal[44]	51.54
Residual SamLa coal[45]	86.95
Residual SamLa coal treated with (H_3PO_4)[46]	256.4
Rice husk[47]	15.31
Rice husk char[15]	39.21
Petroleum coke[15]	11.06
Coke breeze[15]	4.64
Commercial activated carbon[15]	526.31
Microporous cyclodextrin[44]	167.0
Charred saw dust[45]	147.0
Modified Bentonite[46]	139.4
Modified starch[47]	131.5
Silica beads[48]	116
Bagasse fly ash[41]	8.3
Zeolite[49]	1.02
Pyrolyzed residue from animal bones[50]	111.0
Pyrolyzed oil shale[51]	4.895
$ZnCl_2$ pyrolyzed oil shale[51]	6.026
KOH pyrolyzed oil shale[51]	0.895

Conclusions

In this study, the adsorption potential of phosphoric acid activated tea waste was investigated for the removal of *p*-nitrophenol. The Langmuir model fits the experimental data very well, indicating monolayer coverage of *p*-NP molecules at the outer surface of ATW. A maximum adsorption capacity of 142.85 $\text{mg}\cdot\text{g}^{-1}$ was exhibited by ATW. The pseudo-second-order kinetic model was found to represent the experimental data better than the pseudo-first-order model. The efficiency of ATW for *p*-NP adsorption is also ascertained by the rapid uptake of adsorbate within the first 1 h of adsorption. The adsorption process was controlled solely by intraparticle diffusion. The adsorption mechanism follows a Fickian mechanism of diffusion. Studies on the influence of other anions, such as chloride, nitrate, and sulfate, showed a negative effect on the removal of *p*-NP. The results demonstrated that industrial tea waste, which has a very low economic value, may be used effectively in the removal of *p*-NP from aqueous systems for environmental cleaning purposes.

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Received for review February 2, 2010. Accepted May 16, 2010.

JE100117S